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THIONES AND THIALS

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Received November 23, 1945

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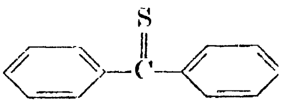
I. INTRODUCTION

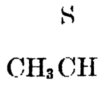
The thiones and thials are compounds of the structure, $R\overset{\overset{S}{\|}}{C}R'$, where R and R′ may be hydrogen, or alkyl or aryl groups. However, the tendency of the thiocarbonyl group to trimerize or polymerize is so great that it is necessary to include those compounds which can be illustrated by the formula $(RCSR')_n$, where n is 1, 2, or 3, or by the formula $HS(RCSR')_xH$, where x is any number, usually greater than 3.

II. NOMENCLATURE

Compounds of this type have been given a variety of names in the early literature. Thiobenzaldehyde has been called "sulfurbenzene" (43, 64) and dithioacetone was referred to as "duplosulfacetone" (223). The Geneva System requires the use of the suffixes "thial" and "thione" to indicate the thioaldehydes and thioketones (151). For example, thioacetone is "propanethione" and thioacetaldehyde is "ethanethial". No provision is made for the naming of the aromatic derivatives. The most common system of nomenclature, and that used here, is to name the compound as the thio derivative of its oxygen analog.



Thiobenzophenone



$CH_3\overset{S}{C}H$

Thioacetaldehyde

The trimers of thials and thiones are sometimes named as derivatives of the trimethylene trisulfide ring (88, 92, 119). In *The Ring Index* (152) preference is given to s-trithiane. However, the relation of the monomers, dimers, trimers, and polymers is more clearly indicated by the most commonly used system of naming them as multiples of the parent thiocarbonyl compound. For example:

$(CH_3CSCH_3)_2$	$(C_6H_5CSCH_3)_3$	$HS(CH_2S)_xH$
Dithioacetone	Trithioacetophenone	Polythioformaldehyde

The general class of compounds usually referred to as thioketones has been indexed since 1938 by *Chemical Abstracts* under the name "thiones", as suggested by the Definitive Report of the Commission on the Reform of the Nomenclature of Organic Chemistry (152). Since this same report suggests "thials" for thioaldehydes, this term has been used here, although *Chemical Abstracts* uses "aldehydes, thio" for indexing.

These compounds have been briefly discussed by Connor, in his chapter on "Organic Sulfur Compounds," in Gilman's *Organic Chemistry* (50). The monomeric diaryl and heterocyclic thiones have been reviewed by Schönberg (174).

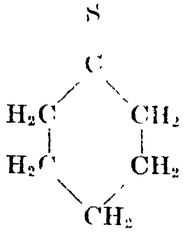
III. Classification

The thials may be divided into two main groups:

A. The alkyl thials, RCHS, and
B. The aryl thials, ArCHS.

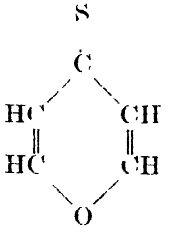
The thiones may be divided into five principal types:

C. Dialkyl thiones, RCSR′,
D. Alkyl aryl thiones, ArCSR,
E. Diaryl thiones, ArCSAr′,
F. Homocyclic thiones, like thiocyclohexanone (I), and
G. Heterocyclic thiones, like γ-thiopyrone (II) and thioacridone (III).



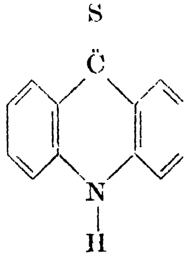
I

Thiocyclohexanone



II

γ-Thiopyrone



III

Thioacridone

IV. Preparation of Thials and Thiones

A. ALKYL THIALS

1. Effect of hydrogen sulfide on aldehydes

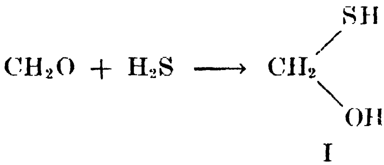
Thioformaldehyde has never been prepared in the monomeric form, and in fact it is highly questionable whether any monomeric alkyl thials have ever been prepared. Methods designed for their synthesis usually lead to the formation of trithials. The most useful and most widely applied method for the preparation of trithials is the treatment of an acid solution of the aldehyde with hydrogen sulfide.

$$RCHO + H_2S \rightleftharpoons RCHS + H_2O$$
$$3RCHS \rightarrow (RCHS)_3$$

This reaction was first applied to the preparation of thioformaldehyde in 1868 by Hofmann (93), who obtained a compound which melted at 218°C. and for which he suggested the formula $(CH_2S)_n$, which was later (95, 158) changed to $(CH_2S)_3$. Bost and Constable (38) report yields of 92-94 per cent of trithioformaldehyde when hydrogen sulfide is passed for 12 to 24 hr. into a tall cylinder containing a solution of formaldehyde in concentrated hydrochloric acid.

In addition to trithioformaldehyde, a variety of other products have been isolated from this reaction. Baumann (11) isolated a compound which corresponded to the formula $(CH_2S)_3CH_2O$. No structure was assigned to this substance, although it was also obtained by Drugman and Stockings (54) when hydrogen sulfide was passed into a neutral solution of formaldehyde. A highly insoluble amorphous white powder, called thiometaformaldehyde, was produced by treating a solution of hexamethylenetetramine with hydrogen sulfide and ammonia (Wohl (224)). Baumann and Fromm (20) also isolated this product, melting at 175–176°C., and assigned to it the polymeric formula $(CH_2S)_x$. Fromm and Soffner (71) describe a dimercaptan melting at 216°C. to which the structure $HS(CH_2S)_xH$ has been assigned.

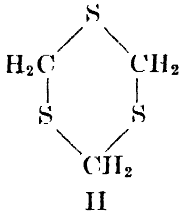
Baumann (11) proposed a mechanism for the reaction between hydrogen sulfide and aldehydes which accounted for the formation of these compounds. In the first step, hydrogen sulfide adds to formaldehyde.



$$CH_2O + H_2S \longrightarrow CH_2(SH)(OH)$$

I

Three molecules of I may then react to give the trimer (II) and water, or they

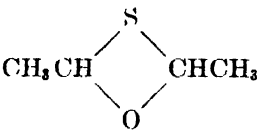


II

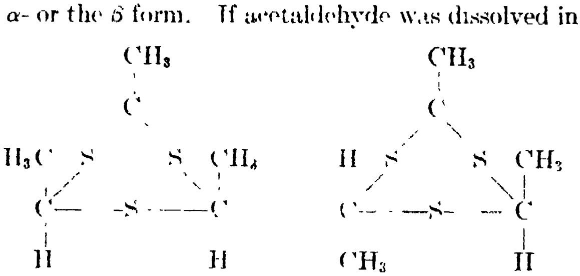
may polymerize to give $HSCH_2SCH_2SCH_2OH$ or larger molecules (20). A high concentration of hydrogen ion seems to catalyze the trimerization. At the present time, it would seem that any confusion in the properties of compounds formed in the treatment of formaldehyde with hydrogen sulfide is due to the existence of polymers of the formulas:

$$HS(CH_2S)_xH \qquad HS(CH_2O)_x(CH_2S)_yH \qquad HO(CH_2O)_x(CH_2S)_yH$$

The preparation of thioacetaldehyde has also been studied extensively. In 1848, Weidenbusch (221) described a water-insoluble oil produced by treating an aqueous solution of acetaldehyde with hydrogen sulfide. Treatment of this oil with acid gave white crystals which sublimed at 45°C. and had the composition $C_4H_4S_2$. Pinner (155) also obtained a low-melting oil by treating acetaldehyde with hydrogen sulfide in aqueous solution; this oil may have been a complex of thioacetaldehyde and acetaldehyde with the structure:



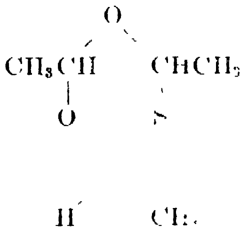
When this oil was treated with concentrated hydrochloric acid, thioacetaldehyde, of indefinite melting point, was obtained. Klinger (105, 107) reinvestigated these products more carefully and isolated an insoluble oil, to which the formula $(C_2H_4S)_8 \cdot H_2S$ was assigned. Treatment of this oil with strong acids, or acidification of the original aldehyde solution before addition of the hydrogen sulfide, gave a white crystalline mass which could be separated by recrystallization into two compounds: one melting at 101°C. and designated α-trithioacetaldehyde; the other melting at 125–126°C. and called β-trithioacetaldehyde. Since molecular-weight determinations showed them both to have the formula $(CH_3CHS)_3$, Klinger pointed out that they may be *cis-trans* isomers. By controlling the conditions, Baumann and Fromm (15) found it possible to prepare either the α- or the β form. If acetaldehyde was dissolved in ethyl alcohol



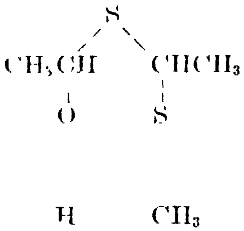
cis *trans*

and this solution saturated with dry hydrogen chloride and hydrogen sulfide at 0°C., the β-form, m.p. 125–126°C., was obtained. If the reaction was run at room temperature in hydrochloric acid solution, the α-form, m.p. 101°C., was obtained. On the other hand, Suyver (215) found that when acetaldehyde was dissolved in 2 N hydrochloric acid and hydrogen sulfide added at −15°C., α-trithioacetaldehyde was formed. If concentrated hydrochloric acid was used as a solvent and the reaction run at room temperature, the β-isomer was formed. The α-form may be converted to the β-form by the use of catalysts such as iodine, sulfur trioxide, or hydrogen chloride. Drugman and Stockings (51) isolated the α- and β-forms from an acid solution of acetaldehyde, and also reported a γ-form, m.p. 76°C. The existence of a γ-form is doubtful, however. The question of the absolute configurations of these isomers and of other unsymmetrical thiocarbonyl trimers will be discussed later (Section V, A).

Muller and Schiller (146) attempted to prepare thioacetaldehyde directly from acetylene. A mixture of acetylene and hydrogen sulfide was passed into 63 per cent sulfuric acid containing mercuric sulfate at 30–40°C. The product crystallized in white needles, melting at 78–80°C., and had the composition $(CH_3CHS)_3$. Acetaldehyde was undoubtedly an intermediate in this reaction, however, since monothioparaldehyde (III), melting at 55°C., was also isolated. This compound and dithioparaldehyde (IV), m.p. 70–72°C., had previously been isolated (107, 115, 127). Either of them may be converted to trithioacetaldehyde and acetaldehyde by treatment with strong acids.



III
Monothioparaldehyde



IV
Dithioparaldehyde

Little effort has been made to prepare any alkyl thials of higher molecular weight, either by the use of hydrogen sulfide or by other methods. By the reaction between *n*-valeraldehyde and aqueous hydrogen sulfide Schroder (194) had isolated a compound of very unpleasant odor and melting at 69°C., to which was assigned the monomeric formula $C_5H_{10}S$. The color of the compound was not mentioned. About the same time, Pfeiffer (154) treated isobutyraldehyde with hydrogen sulfide and obtained an oil which could be steam distilled, but was not further purified. It had an unpleasant onion-like odor.

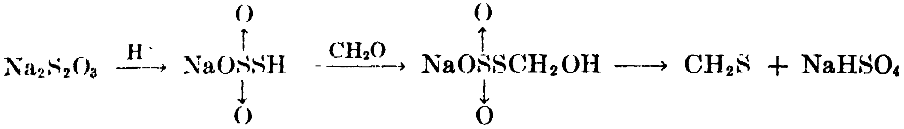
Drugman and Stockings (54) discuss the effect of hydrogen sulfide on propionaldehyde and isobutyraldehyde, but did not isolate any pure products.

A recent German patent (147) deals with the preparation of unsaturated aliphatic thioaldehydes by treating the unsaturated aldehyde with hydrogen sulfide in a neutral medium, but no specific examples are given. Poleck and Thrummel (158) claim to have isolated the γ-trithioacetaldehyde, m.p. 75–76°C., by treating vinylmercuryoxychloride, $CH_2{=}CHO_2Hg_2Cl_2$, with hydrogen sulfide. They give the following equation for the reaction:

$$6C_2H_3Hg_2O_2Cl_2 + 21H_2S \rightarrow 2(CH_3CHS)_3 + 12HCl + 12H_2O + 3Hg_2S + 12HgS$$

2. *Action of sodium thiosulfate on aldehydes*

Although the use of hydrogen sulfide has been most widely studied, aliphatic thioaldehydes have been obtained by a number of different methods. Vanino (217, 218) found that addition of hydrochloric acid to a solution of sodium thiosulfate in formalin produced a mixture of sulfur and trithioformaldehyde. The yield was not reported, but the following mechanism for the reaction was proposed:

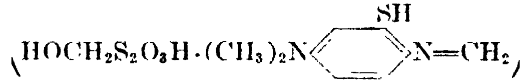


$$Na_2S_2O_3 \xrightarrow{H^+} NaO\overset{O}{\overset{\uparrow}{\underset{\underset{O}{\downarrow}}{S}}}SH \xrightarrow{CH_2O} NaO\overset{O}{\overset{\uparrow}{\underset{\underset{O}{\downarrow}}{S}}}SCH_2OH \longrightarrow CH_2S + NaHSO_4$$

$$3CH_2S \longrightarrow (CH_2S)_3$$

When paraldehyde was used in this reaction a compound was obtained which analyzed for $(CH_3CHS)_3$, but it could not be purified.

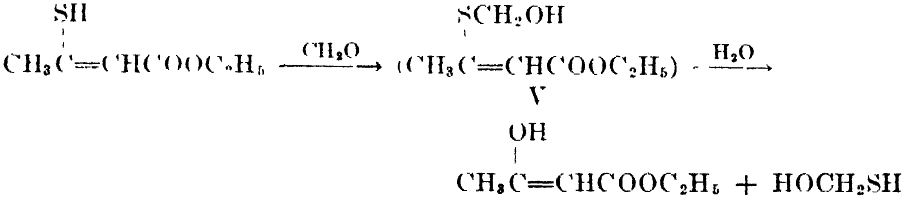
This reaction was also investigated by Schmidt (169, 170), who was able to isolate a salt of the intermediate acid, $HOCH_2SSO_3H$, postulated by Vanino. When a solution containing 2-amino-5-dimethylaminothiophenol dissolved in ammonium hydroxide was mixed with sodium thiosulfate and formalin, and acidified with hydrochloric acid, white plate-like crystals were deposited. This compound melted at 122°C., analyzed for $C_{30}H_{48}N_6S_9O_{12}$, and upon treatment with sodium hydroxide produced formaldehyde, sodium thiosulfate, and a polymeric anhydroformaldehyde-2-amino-5-dimethylaminothiophenol. Schmidt therefore proposed the following structure for the salt:



Although both Vanino and Schmidt report that this reaction works with water-soluble aldehydes other than formaldehyde, no compounds except trithioformaldehyde have been reported.

3. Reaction of thioacetoacetic esters with aldehydes

S. K. Mitra investigated the β-thioketonic esters (136, 143) extensively, and found that these compounds condensed with aldehydes in the presence of acids and a trace of moisture to form the trithioaldehydes and the ketonic esters. Mitra utilized this reaction to prepare a number of aryl thials, but only one alkyl thial trithioformaldehyde (142). Trithioformaldehyde, m.p. 218°C., was obtained when an alcohol solution of ethyl thioacetoacetate which had been saturated with dry hydrogen chloride at 0°C. was treated with a 10 per cent solution of formaldehyde, heated on a steam bath, and let stand overnight. Mitra suggests, as a mechanism, addition of the thiol phase of the ester to the aldehyde, and subsequent hydrolysis of the hydroxymethylthioether formed.



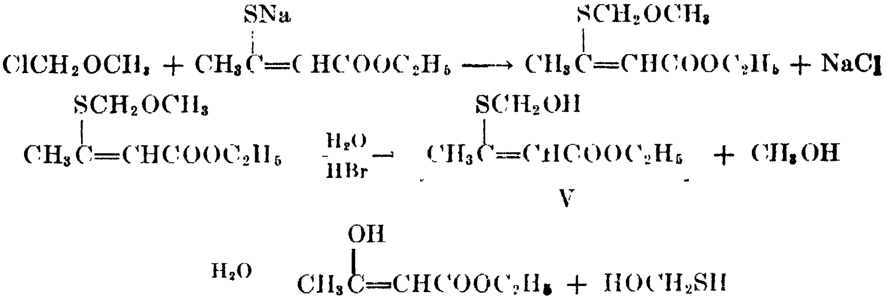
$$CH_3\overset{SH}{\overset{|}{C}}=CHCOOC_2H_5 \xrightarrow{CH_2O} (CH_3\overset{SCH_2OH}{\overset{|}{C}}=CHCOOC_2H_5) \xrightarrow{H_2O}$$

$$\downarrow$$

$$CH_3\overset{OH}{\overset{|}{C}}=CHCOOC_2H_5 + HOCH_2SH$$

$$3HOCH_2SH \longrightarrow (CH_2S)_3 + 3H_2O$$

This is similar to the mechanism proposed by Baumann (11) for the reaction of hydrogen sulfide with aldehydes. As evidence in support of this mechanism, Mitra found that the reaction required a trace of moisture, and he was also able to prepare the methyl ether of the hypothetical ethyl β-hydroxymethylmercaptocrotonate (V) (142). A mixture of chloromethyl ether and ethyl sodiothioacetoacetate was refluxed in benzene for 6 hr., to give the ethyl β-methoxymethylmercaptocrotonate, $C_8H_{14}SO_3$, b_{12} 120°C. Hydrolysis of this oil with concentrated hydrobromic acid at room temperature gave trithioformaldehyde.



$$ClCH_2OCH_3 + CH_3\overset{SNa}{\overset{|}{C}}=CHCOOC_2H_5 \longrightarrow CH_3\overset{SCH_2OCH_3}{\overset{|}{C}}=CHCOOC_2H_5 + NaCl$$

$$CH_3\overset{SCH_2OCH_3}{\overset{|}{C}}=CHCOOC_2H_5 \xrightarrow[HBr]{H_2O} \underset{V}{CH_3\overset{SCH_2OH}{\overset{|}{C}}=CHCOOC_2H_5} + CH_3OH$$

$$\xrightarrow{H_2O} CH_3\overset{OH}{\overset{|}{C}}=CHCOOC_2H_5 + HOCH_2SH$$

$$3HOCH_2SH \longrightarrow (CH_2S)_3 + 3H_2O$$

The same reaction occurred when ethyl α-isobutylthioacetoacetate was used in place of ethyl thioacetoacetate.

4. Reaction of sulfides with alkyl halides

A well-known method of preparing mercaptans is to treat an alkyl halide with a metal sulfide or bisulfide. Husemann (98) attempted to apply this reaction to the preparation of thioformaldehyde.

$$CH_2I_2 \xrightarrow{NaHS} CH_2(SH)_2 \longrightarrow CH_2S + H_2S$$

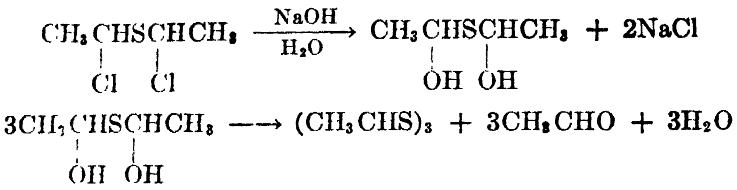
When methylene iodide was refluxed with sodium bisulfide in alcohol, a white powder was obtained which sublimed at 150°C. The compound had many of the reactions of trithioformaldehyde, forming addition products with metal salts and oxidizing to a sulfoxide. Husemann called it dimethylenesulfur and assumed it to be $(CH_2S)_x$. It behaved like a compound prepared by Girard with the empirical formula CH_2S (76).

The trithioaldehydes are obtained when α,α′-dichlorodialkyl sulfides are hydrolyzed. Block and Hohn (36) obtained trithioformaldehyde when dichlorodimethyl sulfide was treated with water.

$$ClCH_2SCH_2Cl + 2H_2O \rightarrow HOCH_2SCH_2OH + 2HCl$$

$$3HOCH_2SCH_2OH \rightarrow (CH_2S)_3 + 3CH_2O + 3H_2O$$

Mann and Pope (125) obtained the γ-trithioacetaldehyde, m.p. 81°C., when α,α′-dichlorodiethyl sulfide was treated with silver sulfide, hydrogen sulfide, silver oxide, or sodium hydroxide. These reactions are probably similar to the hydrolysis of the dichlorodimethyl sulfide.



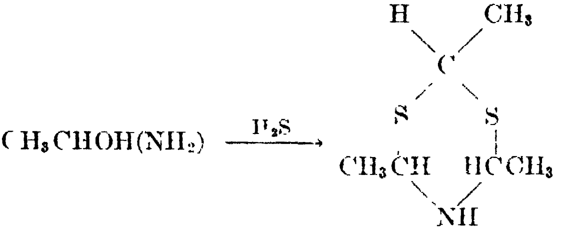
$$\mathrm{CH_3\underset{Cl}{CH}S\underset{Cl}{CH}CH_3 \xrightarrow[H_2O]{NaOH} CH_3\underset{OH}{CH}S\underset{OH}{CH}CH_3 + 2NaCl}$$

$$\mathrm{3CH_3\underset{OH}{CH}S\underset{OH}{CH}CH_3 \longrightarrow (CH_3CHS)_3 + 3CH_3CHO + 3H_2O}$$

These same authors (126) noted that β-trithioacetaldehyde was obtained when diethylidene trisulfide, $(CH_3CH)_2S_3$, was treated with methyl iodide. None of these methods are useful preparative methods, since the α,α′-dichlorodialkyl sulfides and diethylidene trisulfide are prepared from the trithioaldehydes originally.

5. Special preparations

(a) *Thialdine thiocyanate:* Marckwald investigated the decomposition of thialdine thiocyanate (127). Thialdine (VI) was prepared by passing hydrogen sulfide into a solution of aldehyde ammonia. The thiocyanate was made from it by treating a solution of thialdine hydrochloride with excess potassium thiocyanate.



VI

Thialdine

$$\mathrm{VI\cdot HCl \xrightarrow{KSCN} VI\cdot HSCN}$$

$$\mathrm{VI\cdot HSCN \xrightarrow{H_2O} (CH_3CHS)_3}$$

Boiling this salt with water caused it to decompose, and crystals of the γ-trithioacetaldehyde, m.p. 76°C., were obtained The γ-isomer was also obtained from methylthialdine thiocyanate (128). Marckwald noted (127, 129) that the γ-isomer could be converted to β-trithioacetaldehyde by treatment with concentrated sulfuric acid or ethyl iodide.

(b) *Reduction of carbon disulfide:* In 1856, Girard (76) isolated a white crystalline compound, which sublimed at 150°C. and decomposed at 200°C., by reducing carbon disulfide with zinc and hydrochloric acid. This compound was soluble in organic solvents, insoluble in water, and gave addition complexes with silver, gold, mercury, and platinum salts. The analysis corresponded closely to that calculated for CH_2S. Husemann (98) later prepared the same compound by a different method, as already noted. It is probably a thioformaldehyde polymer.

(*c*) *Reduction of ethyl isothiocyanate:* Hofmann (94) obtained trithioformaldehyde by reduction of ethyl isothiocyanate with zinc and hydrochloric acid.

$$3C_2H_5NCS \xrightarrow[HCl]{Zn} 3C_2H_5NH_2 + (CH_2S)_3$$

(*d*) *Pyrolysis of mercaptals:* Schönberg and Schutz (187) were unable to prepare thioformaldehyde compounds by heating the dibenzylmercaptal of formaldehyde, although aryl thials and thiones could be obtained by heating the corresponding aryl mercaptals or thioketals.

(*e*) *Heating glycerol with sulfur.* Delson (52) has patented a process for making thioacrolein by heating sulfur with glycerol at 175–200°C. for 1–1½ hr. in a steel retort under pressure. The patent does not describe the characteristics of $CH_2{=}CHCHS$, but notes that the compound is germicidal and non-poisonous.

B. ARYL THIALS

The aryl thials have been investigated rather thoroughly. In particular, Worner (228) has studied the substituted trithiobenzaldehydes and prepared a large number of new compounds. He was particularly interested in obtaining both the α-, or *cis*, and β-, or *cis–trans*, isomers of each compound. Frequently, only one isomer can be obtained. This is regarded as the β- or *cis–trans* isomer, because the β-isomer is always the most stable and least soluble of the two isomers when both are known, and in preparations in which both isomers are formed, the β-form usually is heavily predominant.

In addition to the trithials, a number of arylpolythials have been obtained. The molecular weights of some of the polythiobenzaldehydes have been found, but in the other cases the compounds have been too insoluble for molecular-weight determinations. No pure monomeric aryl thials have been described.

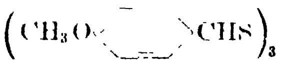
1. Action of hydrogen sulfide on aldehydes

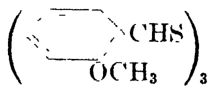
This method has been most extensively applied in this series of thiocarbonyl compounds. The earliest report is probably that of Bertagnini (34), who noted in 1851 that when hydrogen sulfide was passed into "nitrated benzaldehyde" in alcohol solution, an amorphous, highly insoluble white powder was obtained. This was undoubtedly the same polymeric *m*-nitrothiobenzaldehyde prepared much later by Mitra in another way (137). Klinger (105) was the first to prepare β-trithiobenzaldehyde, by passing dry hydrogen chloride and hydrogen sulfide into a solution of benzaldehyde in absolute alcohol. The product, to which the formula $(C_6H_5CHS)_n$ was assigned, melted at 225–226°C.

Baumann and Fromm (15, 18) studied the compounds obtained when an alcohol solution of benzaldehyde was treated with hydrogen sulfide and various concentrations of hydrogen chloride. It was noted that the amount of β-isomer was greatly increased as the temperature of the reaction and the concentration of hydrogen chloride increased. Among the products obtained were the two trimers, α-trithiobenzaldehyde, m.p. 167°C., and β-trithiobenzaldehyde, m.p. 225°C. Another product, previously called α-trithiobenzaldehyde, which melted at 83–85°C., was shown to be the same as Laurent's thioaldehyde (114) which melted at 80-90°C. Baumann and Fromm (18) determined the molecular weights of this compound and of another low-melting polymer first prepared by Klinger, and found them to correspond to $(C_6H_5CHS)_{10}$ and $(C_6H_5CHS)_9$, respectively. Suyver (215) also made a careful study of the two isomers, determining the solubilities and extent of conversion of the α- into the β-form by treatment with catalysts. The α-form could be prepared in high yield by diluting an alcohol solution of benzaldehyde with one-fourth its volume of alcohol saturated with hydrogen chloride, cooling this mixture to −15°C., and saturating with hydrogen sulfide. The β-form was obtained by saturating an alcohol solution of benzaldehyde with hydrogen chloride and hydrogen sulfide at 0°C. If the α-trithiobenzaldehyde was heated alone, only a small amount of the β-isomer was formed, but if it was heated with an acid catalyst, such as acetyl chloride, hydrogen chloride, sulfur trioxide, or iodine, it was largely converted to the more stable β-isomer. The α-isomer is 55 times as soluble in chloroform and 435 times as soluble in benzene at 25°C. as the β-isomer.

More recently Wood and Bost (226) have studied the formation of thiobenzaldehyde from benzaldehyde and hydrogen sulfide in alcohol. These authors noted that when the alcohol was saturated with hydrogen chloride, the β-trimer was formed exclusively, but if the concentration of the hydrogen chloride was decreased, gummy linear polymers of thiobenzaldehyde were obtained. If the reaction was run in basic alcohol solution (potassium or sodium hydroxide), a mixture of sulfur compounds, including the salts of benzyl mercaptan and dithiobenzoic acid, as well as thiobenzaldehyde, was obtained. Wood and Bost attempted to prepare monomeric thiobenzaldehyde from the β-trimer by distillation. With a drop of sulfuric acid added, the compound decomposed to give an impure red oil which may have been chiefly monothiobenzaldehyde.

Numerous substituted benzaldehydes have been prepared by the hydrogen sulfide reaction. In addition to the polymeric nitrothiobenzaldehyde of Bertagnini (34), Jackson and White (99) obtained reddish white gummy compounds when *p*-chloro-, *p*-bromo-, or *p*-iodo-benzaldehyde was treated with hydrogen sulfide in alcohol solution without additional acid. These compounds were not further investigated. Baumann and Fromm (19) prepared several alkoxy-substituted trithiobenzaldehydes by treating acidic alcohol solutions of the aldehyde with hydrogen sulfide. Both the α- and the β-forms of trithioanisaldehyde (I), trithiomethylsalicylaldehyde (II), trithioisobutylsalicylaldehyde (III), and trithiocinnamaldehyde (IV) were obtained.


I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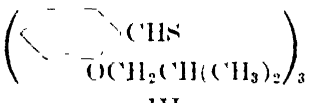
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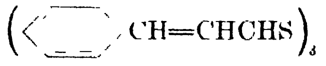
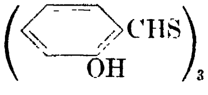
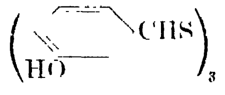

IV

The α-form of I was obtained from an alcohol solution of the aldehyde to which one-tenth of its volume of concentrated hydrochloric acid had been added before saturating with hydrogen sulfide gas

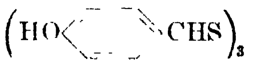
Kopp (111) prepared the trithials of salicylaldehyde (V), *m*-hydroxybenzaldehyde (VI), and *p*-hydroxybenzaldehyde (VII), and their benzoyl esters, but was



V



VI



VII

unable to obtain the α-modification of any of these compounds. Lowering the acid concentration of the reaction gave linear polymers, in the case of the *o*- and *p*-benzoyloxybenzaldehydes, which could be converted to the β-trimer by treatment with acid or iodine. Kopp also attempted to prepare both forms of *m*-methoxybenzaldehyde, but was only able to obtain the β-form, m.p. 147°C., and a linear polymer, m.p. 95–97°C.

Worner (228) carried on Baumann's original idea in attempting the isolation of the *cis*- and *trans*-isomers of numerous substituted benzaldehydes by the method of lowering the acid concentration and the temperature of the reaction in order to promote the formation of the α-isomer. This gave mixtures of the two isomers, which could then be separated by fractional crystallization. Worner was able to make several generalizations based on the data obtained. Like Kopp, he was unable to obtain the α-forms of trithiosalicylaldehyde, trithio-*m*-hydroxybenzaldehyde, trithio-*p*-hydroxybenzaldehyde, trithiovanillin, and trithiogentisinaldehyde Also, only the β-forms of the benzoyl derivatives of the first four were obtained. (No attempt was made to prepare the dibenzoyl derivative of thiogentisinaldehyde.) The nitrobenzaldehydes gave linear polymers, while *m*-nitroanisaldehyde, 3,5-dinitroanisaldehyde, and *m*-nitrocuminaldehyde yielded only the β-trithio derivatives.

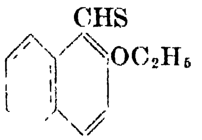
However, when alkyl groups or halogen groups were substituted in benzaldehyde, both the α- and the β-trithio isomers were readily isolated. Also, if the hydrogens of the hydroxyl groups in the hydroxybenzaldehydes were replaced by alkyl groups, as in methylsalicylaldehyde, isobutylsalicylaldehyde, anisaldehyde, *p*-benzyloxybenzaldehyde, methylvanillin, piperonal, or dimethylgentisinaldehyde, both isomers were obtained, except in the case of *m*-methoxybenzaldehyde.

Worner made the following generalizations: (*1*) Substituted aromatic aldehydes give two isomeric trithials only when the substituent is positive or neutral. When it is negative, the lower-melting α-form is not obtained When the acidity of the phenol group is masked by methyl or benzyl, both isomers are obtained, but benzoylation gives only the β-isomer. (*2*) The phenolic aldehydes give only the β- or *cis–trans* trithials. (*3*) Trithials are generally easier to prepare when positive substituents are present When negative substituents are present, the tendency is to form high polymers.

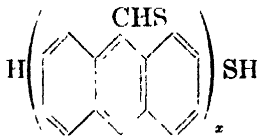
The absence of the α trithio-*m*-methoxybenzaldehyde has not been explained.

Several obvious tests of Worner's hypotheses should be made. The substitution of a benzoyl group for hydrogen in the hydroxyaldehydes may have a volume effect which would prevent the formation of the *cis*-isomer. This is contraindicated by the existence of only one *p*-benzoyloxybenztrithial, but both *p*-benzyloxy isomers. However, more light would be shed on the situation by the preparation of the *o*- and *m*-benzyloxy isomers, and the preparation of the various acetyl derivatives. It would be interesting to test the value of positive substituents by reacting the three aminobenzaldehyde hydrochlorides with hydrogen sulfide in alcohol. The strongly positive ammonium substituent should greatly influence the reaction.

Wood and Bost (227) attempted to prepare monomeric aryl thials by increasing the size of the aryl group, and obtained a red solution of 2-ethoxy-1-naphthial (VIII) which slowly trimerized to the β-form, m.p. 283°C. The 9-anthracenealdehyde, on treatment with hydrogen sulfide or hydrogen sulfide and hydrogen chloride, gave only intractable linear polymers (IX) of indefinite melting point. The authors attribute this to the volume effect of the anthracene nucleus. Later, Wood and coworkers (225) described the preparation of linear polymers of α-naphthial, β-naphthial, 3-phenanthrylthial, and 2-methoxy-1-phenanthrylthial, using hydrogen sulfide and hydrogen chloride with alcohol, or mixtures of alcohol and benzene or ethyl acetate and benzene, as solvents. The trimers could not be isolated in these preparations.



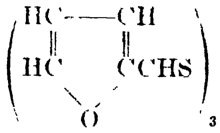
VIII



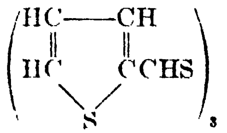
IX

Trithiomesitaldehyde, m.p. 186–187°C., was prepared by Fuson and Best (73) from the aldehyde in cold absolute alcohol, saturated with hydrogen sulfide and hydrogen chloride. Only one isomer was obtained, which was probably the β- or *trans* form.

Both isomers of trithiofurfuraldehyde (X) and trithio-2-thiophenaldehyde (XI) have been prepared by the hydrogen sulfide reaction with the aldehyde. The first was isolated by Baumann and Fromm (21), who reported the β-trithiofurfuraldehyde to precipitate as black needles from chloroform, while the α-isomer was colorless. Steinkopf and Jakob (213) prepared the thiophene compounds, and separated the isomers by fractional crystallization from benzene.



X



XI

2. Action of thioacetoacetic esters on aldehydes

Mitra used the method of reacting aldehydes and thioacetoacetic esters both in alkaline medium (137) and in the presence of acids (142). Ethyl thioacetoacetate and benzaldehyde condense in piperidine to an oil which solidifies on standing. This solid reacts with various aldehyde reagents to give the benzylidene compounds, and on treatment with hydrogen chloride it is converted to β-trithiobenzaldehyde. Molecular-weight determinations and analyses indicated that this compound is a polymer, $(C_6H_5CHS)_7$. Treatment of anisaldehyde in the same way gave a solid, melting at 73–75°C., which proved to be $(CH_3OC_6H_4CHS)_{11}$. Benzaldehyde and ethyl thioacetoacetate in alcohol, treated with hydrogen chloride, gave β-trithiobenzaldehyde almost quantitatively. Other β-thioketobutyric esters, such as α-methyl- and α-isobutylthioacetoacetic esters, could be used in this reaction, as could diethyl thioacetonedicarboxylate, $CS(CH_2COOC_2H_5)_2$, and thioacetomalonic ester, $CH_3CSCH(COOC_2H_5)_2$. Anisaldehyde and vanillin similarly yielded the β-trithials with these reagents. *o*-Nitrobenzaldehyde yielded a polymeric thial of unknown molecular weight, melting at 168–172°C., which is probably the same as that obtained by Wood and coworkers (225) using the hydrogen sulfide reaction. *m*-Nitrobenzaldehyde gave a similar polythial, melting at 185–190°C. Mitra noted that these various polythials were depolymerized in basic medium, since they gave phenylhydrazones with phenylhydrazine alone or in pyridine.

3. Reaction of benzal halides with metal sulfides

The reaction of benzal halides with metal sulfides should represent a possible

$$RCHCl_2 + Na_2S \rightarrow RCHS + 2NaCl$$

method of synthesizing the aromatic thials. Cahours (43) treated benzal chloride with potassium bisulfide, and obtained a crystalline compound in white needles, melting at 64°C., to which was assigned the formula $C_{14}H_6S_2$ (*sic*) and the name "sulfobenzol." Fleischer (64) performed the same reaction in boiling alcohol and obtained a crystalline solid, melting at 68–70°C. The analysis corresponded to C_7H_6S. These compounds were undoubtedly thiobenzaldehyde polymers. Klinger (108) repeated the reaction, using a slight excess of potassium bisulfide, and isolated benzyl disulfide and dithiobenzoic acid. He suggested that thiobenzaldehyde was an intermediate in this reaction, since

$$3C_6H_5CHCl_2 + 7KSH \rightarrow (C_6H_5CH_2S)_2 + C_6H_5CS_2K + 3H_2S + 6KCl$$

treatment of polythiobenzaldehyde with potassium bisulfide yielded the same products. Since potassium bisulfide provides an alkaline medium, a Cannizzaro reaction may be involved in the formation of these substances.

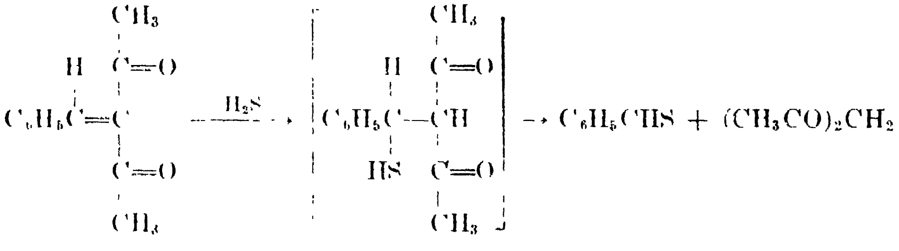
4. Special preparations

(*a*) *Reaction of benzaldehyde with ammonium sulfide:* Laurent (114) studied the products of the reaction of ammonium sulfide or ammonium bisulfide with benzaldehyde, and isolated eight different compounds, most of which contained nitrogen. One of these compounds was a white crystalline solid, melting at 90–95°C., which analyzed correctly for the formula $(C_7H_6S)_n$. Laurent called it hydrosulfobenzoyl, and assumed it to be the dimer. The yield was evidently very low.

(*b*) *Reaction of benzaldehyde with sulfur:* Barbaglia and Marquardt (10) heated benzaldehyde with an equimolar quantity of sulfur at 180°C., and isolated benzoic acid and stilbene from the reaction mixture, along with a small amount of a sulfur-containing compound melting at 164–167°C., which may have been α-trithiobenzaldehyde. These authors suggested that thiobenzaldehyde was an intermediate in the reaction

$$4C_6H_5CHO + 2S \rightarrow 2C_6H_5CHS + 2C_6H_5COOH$$
$$2C_6H_5CHS \rightarrow C_6H_5CH{=}CHC_6H_5 + 2S$$

(*c*) *Action of hydrogen sulfide on benzylideneacetylacetone:* Ruhemann (166) obtained a white crystalline sulfur compound, melting at 75–85°C., when benzylideneacetylacetone was treated with hydrogen sulfide in a warm alcoholic solution containing a small amount of sodium ethoxide. The compound was undoubtedly the polythiobenzaldehyde usually obtained in alkaline solutions. Thiobenzaldehyde is probably first formed by addition of hydrogen sulfide to the double bond, followed by decomposition, and is then polymerized under the influence of the alkali



$$C_6H_5\overset{H}{C}{=}C(COCH_3)_2 \xrightarrow{H_2S} \left[C_6H_5\overset{H}{\underset{HS}{C}}{-}CH(COCH_3)_2\right] \rightarrow C_6H_5CHS + (CH_3CO)_2CH_2$$

$$C_6H_5CHS \xrightarrow{C_2H_5ONa} (C_6H_5CHS)_x$$

(*d*) *Pyrolysis of mercaptals:* As previously noted, Schönberg and Schutz (187) heated a number of alkyl and aryl mercaptals and thioketals to form the thiocarbonyl compounds. The dibenzyl mercaptal of benzaldehyde is reported to be very heat stable, but no figures are given as to temperature or yield in this reaction.

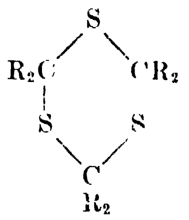
C. DIALKYL THIONES AND SUBSTITUTED DIALKYL THIONES

1. *Action of hydrogen sulfide on ketones*

The simple ketones, acetone (14) and ethyl methyl ketone (119), have been shown to react with hydrogen sulfide in the presence of hydrogen chloride to produce thiones which immediately trimerize. In the case of acetone a second compound, $C_{15}H_{28}S_4$, was also isolated by Baumann and Fromm (14) as well as

$$R_2CO + H_2S \xrightarrow{HCl} R_2CS + H_2O$$
$$3R_2CS \rightarrow (R_2CS)_3$$

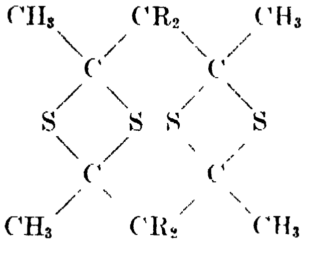
the trimer, $(CH_3CSCH_3)_3$. Presumably these trimers possess the cyclic structure I, analogous to the trithials.



I

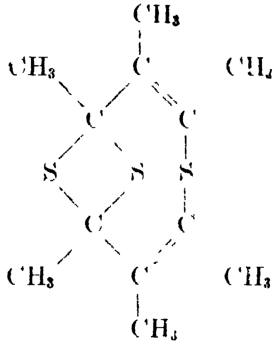
An unsaturated ketone, such as dibenzalacetone, has been found to produce a compound, $C_{20}H_{23}NS_2$, upon treatment with ammonia and hydrogen sulfide (68, 69). Its structure has not been established.

Diketones, such as acetylacetone, also react with hydrogen sulfide in the presence of hydrogen chloride to form very stable dimers to which the cyclic structure IIa has been assigned (72). Dimethylacetylacetone gave an analogous compound of formula IIb, but monomethylacetylacetone, hydrogen sulfide, and hydrogen chloride led to the formation of a more reactive compound, to which structure III was assigned (72).



II

a: R = H
b: R = CH_3

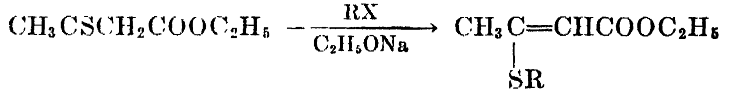


III

β-Thioketo esters are formed in 85 per cent yields when a cold alcoholic solution of β-keto ester is treated with hydrogen sulfide and hydrogen chloride (138). Ethyl thioacetoacetate is an orange liquid with a pleasant odor, and boils at 75–80°C. at 12 mm. pressure. It can be purified by precipitation of a lead salt, which is easily decomposed by hydrogen sulfide. Ethyl thioacetonedicarboxylate was obtained from the corresponding ketone in 75 per cent yield by this method. It is also a pleasant-smelling, rose-red liquid. Similarly, the α-methyl, α-ethyl-, and α-isobutyl-acetoacetic esters yielded the corresponding thio derivatives in good yield, as did acetylmalonic ester.

Mitra attempted to use these compounds in acetoacetic ester condensations,

(a) $$CH_3COCH_2COOC_2H_5 \xrightarrow[C_2H_5ONa]{RX} CH_3COCHRCOOC_2H_5$$

(b) 

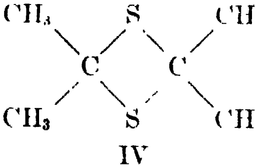
$$CH_3CSCH_2COOC_2H_5 \xrightarrow[C_2H_5ONa]{RX} CH_3\underset{\displaystyle SR}{\underset{|}{C}}{=}CHCOOC_2H_5$$

(a), but found in every case that the vinyl thioether was obtained, indicating that the reaction proceeded as in (b).

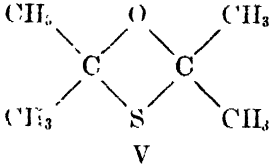
The compounds are probably entirely converted to the thiol form in an alkaline medium.

2. Action of phosphorus sulfides on ketones

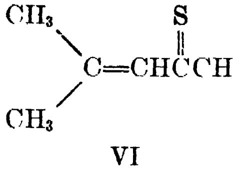
This method has been used frequently in synthesizing the thiones. As early as 1869, Wislicenus (223) obtained dithioacetone (IV), $C_6H_{12}S_2$, by treating acetone with phosphorus pentasulfide. Baumann and Fromm (14) later prepared this same compound and found it to be different from their trimeric thioacetone, which could be converted into the dimer by heating to 200°C. Spring (204) reinvestigated the action of phosphorus pentasulfide on acetone, and isolated methyl mercaptan, isopropyl mercaptan, oxythioacetone (V), and perhaps mesityl sulfide (VI) from the reaction, in addition to dithioacetone (IV). The compound called mesityl sulfide had the formula $C_6H_{10}S$, but was not clearly characterized, and did not behave toward chemical reagents, such as sodium amalgam, as would a compound of structure VI. In addition, Spring found some evidence that thiophorone (VII) may have been formed in the reaction.



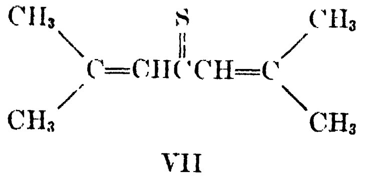
IV
Dithioacetone



V
Oxythioacetone



VI
Mesityl sulfide



VII
Thiophorone

This assumption was based on the isolation, upon the oxidation of crude residues with nitric acid, of a nitrososulfonic acid of unidentified structure and the formula $C_9H_{10}SO_3H \cdot (NO)_2$.

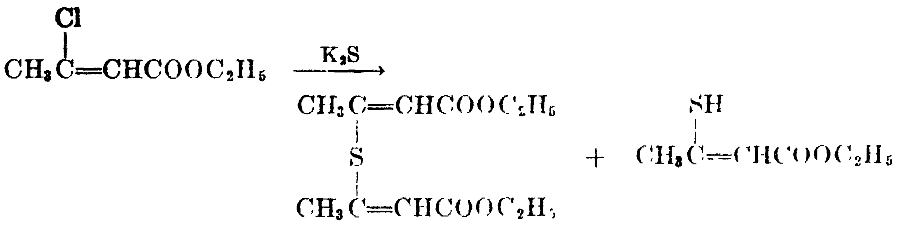
Phosphorus trisulfide was used by Autenrieth (6), who isolated dithioacetone from the reaction of the trisulfide with acetone in a sealed tube. Kretov and Komissarov (113) refluxed powdered phosphorus pentasulfide with various ketones in toluene, and isolated and purified the thiones or dithiones by distillation. These authors note that, in all cases, small yields of impure products were obtained. The ketones used were acetone, ethyl methyl ketone, diethyl ketone, di-*n*-propyl ketone, and di-*tert*-butyl ketone. Analyses of the red oils obtained indicated that acetone, ethyl methyl ketone, and diethyl ketone gave dimeric thiones, while di-*tert*-butyl ketone yielded the monomeric di-*tert*-butyl thione. The product of the reaction of phosphorus pentasulfide and di-*n*-propyl ketone was apparently a mixture of monomeric and dimeric thiones.

Bohme, Pfeifer, and Schneider (37) were unable to prepare dithioacetone by the use of either phosphorus trisulfide or phosphorus pentasulfide, and found that heating trithioacetone gave isopropyl mercaptan, rather than the dimeric compound, as reported by Baumann and Fromm (14)

The treatment of 1,4-diketones with phosphorus trisulfide or phosphorus pentasulfide does not result in the formation of the corresponding 1,4-dithiones. The thiones may be intermediates in the reaction, but the final product is the 2,5-disubstituted thiophenes, which are obtained in good yield (150).

3. *Reaction of vinyl halides with metal sulfides*

This reaction has been investigated in connection with the synthesis of thioacetoacetic ester. Scheibler and Bube (167) treated ethyl β-chlorocrotonate with potassium sulfide in alcohol, and obtained a mixture of the sulfide and the vinyl mercaptan The yield of the β-mercaptocrotonic ester (or thioacetoacetate) was greatly increased by the use of excess potassium bisulfide. Later



$$CH_3\overset{Cl}{\overset{|}{C}}{=}CHCOOC_2H_5 \xrightarrow{K_2S} \begin{array}{c} CH_3C{=}CHCOOC_2H_5 \\ | \\ S \\ | \\ CH_3C{=}CHCOOC_2H_5 \end{array} + CH_3\overset{SH}{\overset{|}{C}}{=}CHCOOC_2H_5$$

Scheibler, Tapouzada, and Schulze (168) studied the β-mercaptocrotonic ester, and found it to be a mixture of the *cis* and *trans* isomers, which could be separated by repeated fractionation. These authors found no evidence of a ketone form. The compound was a red oil boiling at 77°C. at 18 mm. pressure, and thus corresponds very closely to the product obtained from ethyl acetoacetate and hydrogen sulfide (137). Mitra also prepared the ethyl thioacetoacetate by the reaction of potassium bisulfide with β-chlorocrotonic ester (136), but the yield in this case (30 per cent) was much lower than that by the hydrogen sulfide hydrogen chloride method. Mitra found that the compound reacted with phenylhydrazine to give phenylmethylpyrazolone, and evolved hydrogen sulfide when reacted with hydroxylamine. These reactions indicate the presence of some keto form. Methyl α-benzyl-β-mercaptocrotonate was prepared by Scheibler and coworkers (168) from the methyl α-benzyl-β-chlorocrotonate and sodium bisulfide. The pure compound obtained by this method was red-orange in chloroform solution, but was not well characterized.

A recent British patent (109) reports the preparation of thiones by treating vinyl halides with sulfides or thiosulfates in alcohol solution, but no details of the compounds prepared are given.

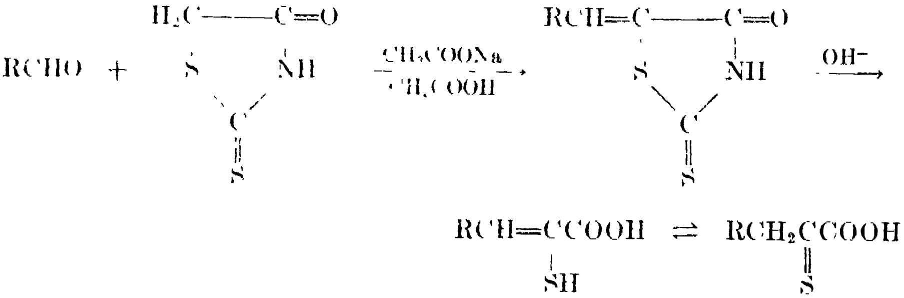
2,2-Dichloropropane has been used to synthesize dithioacetone by Spring (203). The dichloride was treated with sodium thioacetate in alcohol, and the dithioacetate isolated and heated to give the dithioacetone, b.p. 180-185°C. The yield was less than 2 per cent.

$$(CH_3)_2CCl_2 + 2NaSCOCH_3 \xrightarrow[\substack{\text{reflux}\\ \text{60 hr}}]{C_2H_5OH} ((CH_3)_2C(SCOCH_3)_2 + 2NaCl$$

$$2(CH_3)_2C(SCOCH_3)_2 \xrightarrow{\text{heat}} [(CH_3)_2CS]_2 + 2(CH_3CO)_2S$$

5. *α-Thionic acids from aldehydes and rhodanine*

An aldehyde condenses with rhodanine in acetic acid-sodium acetate mixture to give the substituted rhodanine, which on alkaline hydrolysis yields the α-thionic acid (VIII).

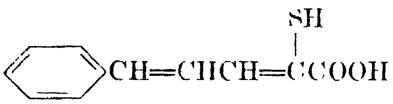


$$RCH{=}\underset{SH}{C}COOH \rightleftharpoons RCH_2\underset{S}{\overset{}{C}}COOH$$

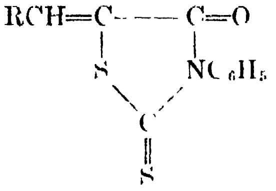
VIII

Zipser (230) treated cinnamylidenerhodanine with barium hydroxide, and obtained α-sulfhydrylcinnamylacrylic acid (IX), which was assumed to occur only in the enol form, since the compound reacted with sodium hydroxide and benzyl chloride to give the benzyl thioether.

Andreasch (1) prepared a number of α-thionic acids by hydrolysis of the corresponding substituted phenylrhodanine compounds (X) with sodium pentoxide.



IV

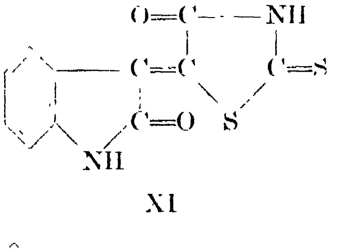


X

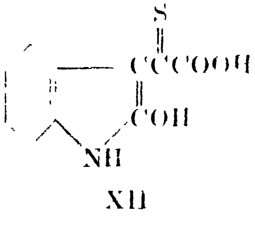
The aldehydes used in the rhodanine condensation which gave stable α-thionic acids were piperonal, vanillin, furfural, *p*-hydroxybenzaldehyde, and *p*-dimethylaminobenzaldehyde. No α-thionic acids could be isolated by alkaline hydrolysis of the rhodanine condensation product formed from *p*-aminobenzaldehyde or *o*-nitrobenzaldehyde.

Granacher (79) studied the properties of phenylthiopyruvic acid (VIII, R = C_6H_5) and found that it gave the same oxime and phenylhydrazone as phenylpyruvic acid, thus indicating the presence of the thione form. Undoubtedly both tautomers exist. Granacher, Gero, Ofner, Klopfenstein, and Schlatter (80) attempted to prepare the aliphatic α-thionic acids from the rhodanine condensation products of acetaldehyde, crotonaldehyde, and isovaleraldehyde, but obtained only intractable oils. These authors obtained a 96 per cent yield of *p*-methoxyphenylpyruvic acid (VIII, R = *p*-$CH_3OC_6H_4$) from anisylidenerhodanine, however. *p*-Isopropylbenzylidenerhodanine yielded an amorphous, intractable solid (VIII, R = *p*-$(CH_3)_2CHC_6H_4$), which reacted with hydroxylamine to give an oxime and hydrogen sulfide.

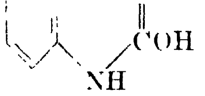
Granacher and Mahal (81) prepared rhodanal-β-oxindole (XI) from isatin and rhodanine. Boiling pyridine converted it readily to the β-oxindolylthionacetic acid (XII), a dark red crystalline solid which on heating gradually softened to a wax-like mass. Compound XII is remarkable for the number of tautomeric forms which are possible. The structure of XII was indicated by conversion to the oxime and reduction to the known β-oxindoleacetic acid (XIII)



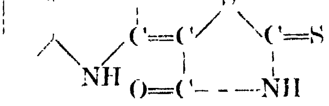
XI



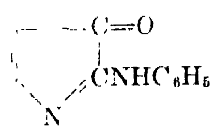
XII



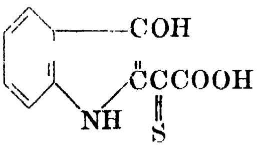
XIII



XIV



XV



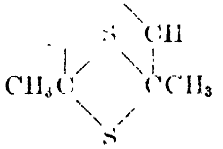
XVI

Rhodanine-2-indolylindigo (XIV) was prepared by condensing isatinanilide (XV) with rhodanine in acetic anhydride. Sodium hydroxide readily converted XIV to α-indoxylylthionacetic acid (XVI), an amorphous red powder, which begins to decompose at 148°C.

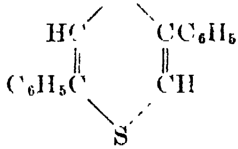
Julian and Sturgis (100) condensed rhodanine with veratraldehyde, and upon alkaline hydrolysis of the product obtained 3,4-dimethoxyphenyl-2-thioketopropionic acid (VIII, R = 3,4-$(CH_3O)_2C_6H_3$). Recently Plucker and Amstutz (157) resynthesized 3-α-furyl-2-thioketopropionic acid (VIII, R = C_4H_4O) by this method and obtained a better yield of higher-melting product than did Andreasch (1).

5. *Special methods*

(a) *Reaction of ketones with carbon disulfide:* Although Bohme, Pfeifer, and Schneider (37) were unable to obtain the simple dimeric thiones by previously reported methods (see above), they were able to prepare a compound containing the four-membered carbon-sulfur ring present in the dimers. Chloroacetone, when treated with carbon disulfide and dry hydrogen chloride, yielded 2,6-dimethyl-2,6-endothio-1,4-dithian (XVII). Acetone reacted with carbon disulfide and anhydrous zinc chloride to give the trithioacetone rather than the dimer. The product of the reaction with α-chloroacetophenone and carbon disulfide was not the expected endothio compound, but 2,5-diphenyl-1,4-dithiene (XVIII). Compound XVIII may be derived from the endothio-

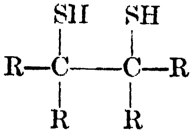


XVII



XVIII

(b) *Action of ammonium sulfide on ketones.* Thiones have not been obtained by the reaction of metal or ammonium sulfides on the ketones. Reduction products are usually obtained from this reaction. Willgerodt (222) treated acetone with ammonium sulfide and obtained a compound which melted at 98°C. and boiled at 243°C., and which was thought to be dithioacetone, but the constants differ from those of either dithioacetone (b.p. 183–185°C.) or trithioacetone (m.p. 24°C.). Manchot and Krische (124) attempted to prepare the dibenzylthione and di-β-phenylethylthione by treating the respective ketones with ammonium sulfide or ammonium bisulfide. The product obtained in each case was the thiopinacol (XIX), in which R = $C_6H_5CH_2$ or $C_6H_5CH_2CH_2$.



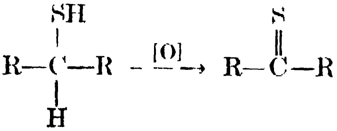
$$R-\overset{\overset{SH}{|}}{\underset{\underset{R}{|}}{C}}-\overset{\overset{SH}{|}}{\underset{\underset{R}{|}}{C}}-R$$

XIX

(*c*) *Treatment of ketone with magnesium bromobisulfide:* Mingoia (135) succeeded in synthesizing trithioacetone by treating anhydrous acetone with magnesium bromobisulfide in absolute ether. The yield was low, however

$$3CH_3COCH_3 + 3MgBrSH \rightarrow (CH_3CSCH_3)_3 + 3MgBrOH$$

(*d*) *Oxidation of mercaptans:* By analogy with the oxygen series, it should be possible to convert the secondary mercaptans to thiones by oxidation, but only one attempt to complete this reaction has been made with the dialkyl thiones.



$$R-\overset{\overset{SH}{|}}{\underset{\underset{H}{|}}{C}}-R \xrightarrow{[O]} R-\overset{\overset{S}{\|}}{C}-R$$

Claus (48) oxidized isopropyl mercaptan with chromium trioxide, and obtained a sulfur-containing compound which boiled at 165–170°C and seemed to be an impure form of Wislicenus' "dithioacetone" (b.p. 183–185°C.).

(*e*) *Pyrolysis of thioketals:* Baumann and Fromm (16) attempted the synthesis of thioacetone from acetone diethylmercaptal by heating, but reported the method not feasible, since there are many side reactions. Similarly, Schönberg and Schutz (187) report acetone dibenzylmercaptal as relatively heat stable.

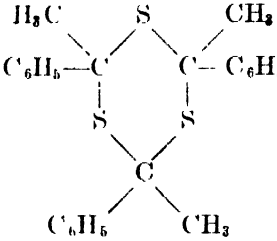
$$3(CH_3)_2C(SC_2H_5)_2 \xrightarrow{160\text{–}190°C.} [(CH_3)_2C{=}S]_3 + 3(C_2H_5)_2S$$

D. ALKYL ARYL THIONES

Very few thiones of this type have been prepared. Trithioacetophenone, which is well characterized, should be a valuable compound in studying the reactions of the thiocarbonyl group. It is a stable trimer below its melting point, but dissociates to the monomer at about 140°C. Thus both forms are readily obtained.

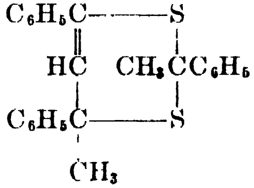
1. *Action of hydrogen sulfide on ketones*

This method is the only one which has received much attention in the preparation of the alkyl aryl thiones. Baumann and Fromm (22) investigated the reaction of acetophenone with hydrogen sulfide and obtained four products. Hydrogen sulfide and dry hydrogen chloride gas were passed into an alcohol solution of acetophenone which was maintained at 0°C. The solution became intense blue-violet in color. The blue monomeric thioacetophenone could not be isolated at this time, however, since it was unstable. After about 24 hr. the reaction mixture had faded in color, and white crystals of trithioacetophenone (I) were deposited. This compound was odorless, and was stable in boiling potassium hydroxide solution or in chloroform containing a trace of iodine. The mother liquors from this preparation were allowed to stand for several days at room temperature, and the crystals which deposited were collected and analyzed. This compound melted at 107-108°C. after recrystallization from alcohol or acetone, and had the formula $C_{24}H_{22}S_2$. Baumann and Fromm proposed the structure II for this compound, and called it anhydrotriacetophenone disulfide. A green resin was also isolated when the reaction was run at slightly higher temperatures, but this substance was not identified.



I

Trithioacetophenone

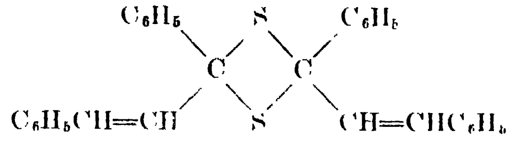


II

Theoretically, two isomers of trithioacetophenone would be expected, the *cis* and the *cis-trans* forms. Only one form was found, which Baumann and Fromm believed to be the more stable *cis-trans* form. The "anhydrotriacetophenone disulfide" (II) may have been formed by loss of hydrogen sulfide from the *cis*-trithioacetophenone. Recently it has been found (44) that if an alcohol solution of acetophenone was first treated with hydrogen chloride, followed by a mixture of hydrogen sulfide and hydrogen chloride, very little trithioacetophenone was formed, but the "anhydrotriacetophenone disulfide" was obtained in good yield. This suggests that dypnone, which is formed when an alcohol solution of acetophenone is treated with dry hydrogen chloride, may be an intermediate substance in the formation of II.

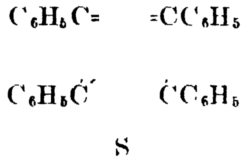
Monomeric thioacetophenone was obtained by Baumann and Fromm (22) on heating trithioacetophenone above its melting point in a vacuum. The compound first melts to a blue oil, which distills as a violet vapor. It was never completely purified, since it decomposed to styrene and hydrogen sulfide when hot, and was partially reconverted to the trimer when cold.

Steinkopf and Jakob (213) treated 2-acetylthiophene with hydrogen sulfide and hydrogen chloride in cold alcohol. They obtained a violet oil which was probably the monomeric 2-thienylmethylthione, but it was not further purified. Fromm (65) treated chalcone with hydrogen sulfide and dry hydrogen chloride in cold alcohol, and obtained a small yield of an unstable crystalline material, which melted at 191°C. and had a molecular weight of 456. It was thought to be the dimeric thiochalcone (III), but the structure was not proven

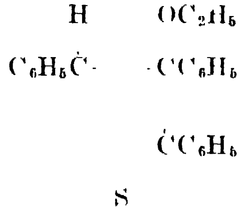


III
Thiochalcone

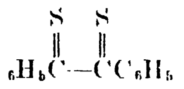
When benzoin was treated with hydrogen chloride and hydrogen sulfide in cold alcohol, a mixture of three compounds was obtained (Mitra (141)). These compounds were separated by crystallization, and their structures proved. They were tetraphenyl-2,5-endothiothiophene (IV), tetraphenyl-3-ethoxy-4-hydro-2,5-endothiothiophene (V), and dithiobenzoin (VI). VI was obtained



IV

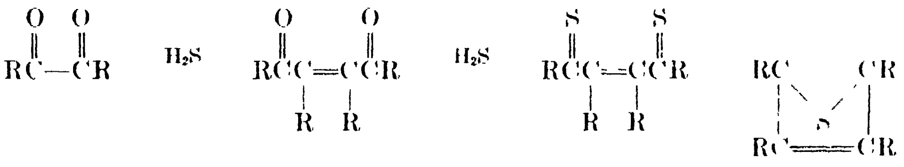


V



VI

in small yield. Mitra investigated the mechanism of the reaction, and concluded that treatment of diketones with hydrogen sulfide first caused condensation to γ-diketones, which are then converted to the dithiones and rearranged to the endothiothiophene derivatives.

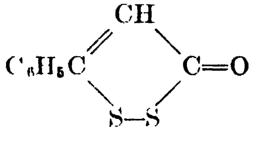


2. *Special methods*

(*a*) *Use of thioacetoacetic esters:* Mitra (137) treated acetophenone with ethyl thioacetoacetate and obtained a deep blue oil, boiling at 110°C. at 20 mm. This was undoubtedly monomeric thioacetophenone.

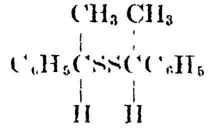
(*b*) *Use of magnesium bromobisulfide:* Mingoia (135) used the reaction of magnesium bromobisulfide with ketones (see above) to prepare trithioacetone. However, when acetophenone was used, the monomeric blue-violet oil was obtained. Distillation caused decomposition and the compound was not further purified.

(*c*) ***Reaction of sulfur with ethyl cinnamate.*** Baumann and Fromm (24) treated ethyl cinnamate with sulfur and obtained the disulfide of thiobenzoylthioacetic acid (VII) in yellow needles, melting at 117°C. Distillation of this compound in vacuum yielded a mixture of monomeric thioacetophenone, 2,4-diphenylthiophene, and hydrogen sulfide.



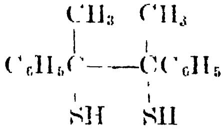
VII

(*d*) *Reaction of ammonium bisulfide on ketones:* Willgerodt (222) had obtained a sulfur-containing compound when acetone was treated with ammonium sulfide, but no sulfur compounds were obtained when aryl ketones like α-naphthylmethyl ketone, acetophenone, or 2,4-dimethylacetophenone were used. Engler (58) treated acetophenone with alcoholic ammonium bisulfide for six weeks, and isolated a solid which crystallized in white needles, melting at 119.5°C. On the basis of analysis, Engler suggested that it was thioacetophenone or a polymer of thioacetophenone. This reaction was checked by Baumann and Fromm (23), who obtained α-phenylethyl disulfide (VIII), melting at 57-58°C., by treating acetophenone with a 65 per cent saturated solution of ammonium bisulfide in alcohol for 8 days. Using various conditions, these authors were unable to obtain any thioketones. Manchot and Krische (124) were able to obtain a compound melting at 118-119°C., $C_{16}H_{18}S_2$, which resembled Engler's preparation from acetophenone and ammonium sulfide in alcohol. This compound was



$$C_6H_5\underset{\displaystyle H}{\overset{\displaystyle CH_3}{C}}SS\underset{\displaystyle H}{\overset{\displaystyle CH_3}{C}}C_6H_5$$

VIII



$$C_6H_5\underset{\displaystyle SH}{\overset{\displaystyle CH_3}{C}}{-\!\!-\!\!-}\underset{\displaystyle SH}{\overset{\displaystyle CH_3}{C}}C_6H_5$$

IX

shown to be the thiopinacol (IX). It is therefore highly improbable that any alkyl aryl thiones have been prepared by the action of ammonium sulfide or bisulfide on the ketones.

E. DIARYL THIONES

The preparation and properties of the diaryl thiones have been extensively investigated, because they exist in the monomeric form only and therefore may be more readily compared to the oxygen analogues. Studies in this series have shown that the thiones behave differently from the ketones in many reactions. A characteristic of the monomeric thiones is that they are all highly colored compounds. Schönberg (190) has reviewed useful methods which have been developed for the preparation and isolation of diaryl thiones.

1. Preparation from diaryl keto chlorides

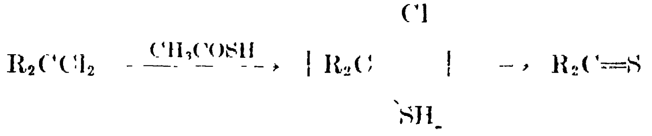
(*a*) *Action of diaryl keto chlorides with metal sulfides:* The preparation of thiobenzophenone has been carried out by Gattermann and Schulz (75), who treated benzophenone dichloride with potassium sulfide in alcohol. A refinement of this method has been described by Staudinger and Freudenberg (209). Benzophenone dichloride was treated with an alcoholic solution of sodium bisulfide

$$\mathrm{C_6H_5CCl_2C_6H_5 + 2NaSH \rightarrow C_6H_5CSC_6H_5 + 2NaCl + H_2S}$$

in an atmosphere of carbon dioxide, causing a vigorous reaction, and the mixture became deep blue in color. The mixture was diluted with water, the thiobenzophenone extracted with ether, and distilled at reduced pressure in an atmosphere of carbon dioxide. The blue oil produced in this way formed beautiful blue crystals, m.p. 53–54°C., on cooling and recrystallizing from the petroleum ether. Thiobenzophenone must be preserved in a sealed glass tube in an atmosphere of carbon dioxide, as it is unstable in the air.

It is interesting to note that Behr (26) reported in 1872 that treatment of benzophenone dichloride with potassium bisulfide in alcohol solution gave a reddish yellow solid which on recrystallization from glacial acetic acid gave snow-white crystals melting at 152–153°C.! This compound analyzed correctly for the formula $\mathrm{C_{13}H_{10}S}$, but no molecular weight was determined. However, when it was heated above its melting point, an intense blue color developed, and oxidation gave benzophenone. The preparation of this compound has never been duplicated, and its identity is unknown. It behaved like the trimeric thioketones of higher molecular weight, however.

(*b*) *Action of diaryl keto chlorides with thioacetic acid:* Schönberg, Schutz, and Nickel (190) described a number of aromatic thiones which were prepared by treating the diaryl keto chloride with thioacetic acid. Most of the thiones could be crystallized directly from the reaction mixture, but thiobenzophenone was purified by distillation in an inert atmosphere. The compounds prepared



$$\mathrm{R_2CCl_2} \xrightarrow{\mathrm{CH_3COSH}} \left[\mathrm{R_2C}\begin{matrix}\mathrm{Cl}\\ \mathrm{SH}\end{matrix}\right] \rightarrow \mathrm{R_2C{=}S}$$

were the *p,p′*-diphenyl-, *p,p′*-dimethoxy-, *o,o′*-dimethoxy-, and *p*-methoxy-*p′*-ethoxy-thiobenzophenones. Kitamura (104) used this method to prepare *p,p′*-diethoxythiobenzophenone.

2. *Preparation by the action of hydrogen sulfide on ketones and ketone derivatives*

Thiobenzophenone was originally prepared by Staudinger and Freudenberg from benzophenone and hydrogen sulfide (207). Passing hydrogen sulfide and hydrogen chloride into a mixture of benzophenone and alcohol in an ice-salt bath for 2–3 hr., followed by hydrogen sulfide for 20 hr., produced deep blue needles of thiobenzophenone in 68 per cent yield, which melted at 51–52°C. after one recrystallization from ligroin. The compound was unstable in air, and was filtered in an atmosphere of carbon dioxide. Steinkopf and Jakob (213) attempted to prepare phenyl-2-thienylthione by passing hydrogen sulfide and hydrogen chloride into a cold alcoholic solution of the ketone. The solution turned violet in color, and after 14 days this color changed to deep green.

Distillation yielded a green oil which was not further identified. Several unsymmetrical thiones were prepared by Bost and Cosby (39), using this method. They found that diphenylphenylthione, phenyl-α-naphthylthione, and phenyl-*p*-tolylthione were all stable monomers which could be produced by this method. However, when a nitro group was substituted in the aromatic ring of the aryl ketones, no thiones were obtained.

Reddelien and Daniloff (162) prepared several diaryl thiones by treating the diaryl ketone anil or anil hydrochloride with hydrogen sulfide. The reaction was complicated by reduction of the thione to the corresponding diarylmethane

$$Ar_2C{=}NC_6H_5 + H_2S \rightarrow Ar_2C{=}S + C_6H_5NH_2$$

by hydrogen sulfide in the reaction mixture. They noted that when a negative substituent, such as the dimethylamino group, was present in the anil, the reaction proceeded much more readily. Thiobenzophenone was obtained in 55 per

$$Ar_2C{=}S + H_2S \rightarrow Ar_2CH_2 + 2S$$

cent yield from benzophenone anil hydrochloride treated with hydrogen sulfide in benzene solution for 6 days, but *p*-dimethylaminobenzophenone anil hydrochloride yielded the corresponding thione in 28 per cent yield on treatment with hydrogen sulfide for 3 hr in boiling benzene. Fehrmann (59) had previously investigated the reaction of hydrogen sulfide on the imine and anil of Michler's ketone and reported yields of 91 per cent and 86 per cent, respectively, but the melting point of the thione was given as 164–166°C., which is about 10°C. lower than that given for *p,p'*-tetramethyldiaminothiobenzophenone by other workers. The compound was not well characterized in other ways by Fehrmann.

3. *Oxidation reactions*

(*a*) *Diarylmethanes with sulfur:* Diaryl ketones may be prepared by the careful oxidation of the corresponding diarylmethane or substituted diarylmethane. Several instances of analogous reactions in the sulfur series have been reported.

$$Ar_2CH_2 \xrightarrow{[O]} Ar_2CO$$

$$Ar_2CHOH \xrightarrow{[O]} Ar_2CO$$

Wallach (220) reported the preparation of Michler's thioketone from *p,p'*-tetramethyldiaminodiphenylmethane by heating the compound with sulfur

$$[(CH_3)_2NC_6H_4]_2CH_2 + 2S \xrightarrow{230°C} [(CH_3)_2NC_6H_4]_2CS + H_2S$$

at 230°C. No yield was given for this reaction. Much later, Tschitschibabin and Knunjanz (216) prepared 2,2'-tetramethyldiamino-4,4'-dipyridylthione in 25 per cent yield by heating the corresponding disubstituted methane with sulfur at 190°C for 5 hr.

(*b*) *Diarylmethanes with polysulfides:* Willgerodt investigated the reaction of polysulfides with various ketones (222) but was unable to prepare thiones by this method. It was noted that in some cases the polysulfides reduced the ketones to methanes. In contrast to this, Badische (7) has patented a method for the production of *N*-alkylated 4,4′-diaminodiaryl thiones by treating the corresponding diaminodiarylmethanes with polysulfides. 4,4′-Tetramethyldiaminothiobenzophenone, 4,4′-dimethyldiamino-3,3′-dimethylthiobenzophenone, and 4,4′-tetraethyldiaminothiobenzophenone were listed as having been prepared by this method, but no constants for the compounds were given.

(*c*) *Leukauramine with sulfur:* Mohlau, Heinz, and Zimmermann (144) have reported that leukauramine, *p*,*p*′-tetramethyldiaminodiphenylmethylamine, was

$$[(CH_3)_2NC_6H_4]_2CHNH_2 + S \rightarrow [(CH_3)_2NC_6H_4]_2CS + NH_3$$

oxidized to Michler's thioketone in 60 per cent yield on heating with sulfur. Although the yield is good, and the product apparently pure (m.p. 202°C.), there seems to have been no attempt to prepare other diaryl thiones by this method, or by oxidation of the diarylcarbinols by sulfur.

(*d*) *Triphenylphosphinediphenylmethylene with sulfur:* Staudinger and Meyer (211) reported that when triphenylphosphinediphenylmethylene was heated with sulfur it gave triphenylphosphine sulfide and thiobenzophenone. The

$$(C_6H_5)_3P{=}C(C_6H_5)_2 + 2S \rightarrow (C_6H_5)_3PS + (C_6H_5)_2CS$$

thiobenzophenone was not isolated, however, but merely identified by color and the preparation of the benzophenone phenylhydrazone.

4. *The Friedel-Crafts reaction*

(*a*) *With thiophosgene:* The preparation of diaryl ketones from phosgene and aromatic compounds by the Friedel-Crafts reaction is common practice. The

$$2ArH + COCl_2 \xrightarrow{AlCl_3} Ar_2CO + 2HCl$$

$$2ArH + CSCl_2 \xrightarrow{AlCl} Ar_2CS + 2HCl$$

analogous reaction in the sulfur series has been well investigated, but is complicated by the difficulty of obtaining pure thiophosgene. Bergreen (23) treated thiophosgene ($CSCl_2$) with aluminum chloride in benzene solution, and obtained an impure red oil, which yielded benzophenone oxime on treatment with hydroxylamine, and benzophenone phenylhydrazone with phenylhydrazine. Gattermann (74) investigated this reaction extensively, using a variety of phenolic ethers, such as anisole or phenetole, as the aromatic reactant, and was able to isolate the corresponding thiones and determine their properties. The yields in these reactions were rather poor.

(*b*) *With trichloromethylsulfur chloride:* Vorlander and Mittag (219) attemped to prepare triphenylmethylsulfur compounds by treating trichloromethylsulfur chloride with benzene and aluminum chloride. Instead of the expected products, thiobenzophenone was obtained in 31 per cent yield

$$C_6H_6 + Cl_3CSCl \xrightarrow{AlCl_3} (C_6H_5)_2CS$$

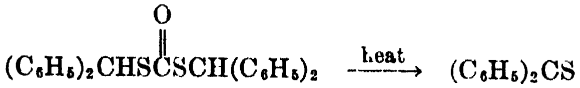
5. Pyrolysis of mercaptals and thioethers

Schönberg and Schutz (184) noted that the mercaptals of aromatic ketones decompose to give highly colored compounds when heated. A later study (187) compared the heat-stability of a large number of aromatic mercaptals, but no attempt was made to purify the resulting thiones, or determine the yields on the various reactions.

Schönberg, Schutz, Bruckner, and Peters (188) noted that certain high-molecular-weight thioethers were thermolabile, decomposing to the thione and methane derivatives. The thioethers therefore differ in their behavior toward heat from the ethers. Thus, tetraphenyldimethyl ether (I) could be distilled at 267°C., but when tetraphenyldimethyl sulfide (II) was heated to this temperature, the color changed and diphenylmethane and thiobenzophenone were obtained. Again the yields on this reaction were too low to be useful preparative methods.

$$\underset{\text{I}}{(C_6H_5)_2CHOCH(C_6H_5)_2} \qquad \underset{\text{II}}{(C_6H_5)_2CHSCH(C_6H_5)_2}$$

Biilman (35) noted that the characteristic color of thiobenzophenone was obtained when diphenylmethyldithiol carbonate was heated.



$$(C_6H_5)_2CHS\overset{\overset{\displaystyle O}{\|}}{C}SCH(C_6H_5)_2 \xrightarrow{\text{heat}} (C_6H_5)_2CS$$

Wuyts (229) obtained thiobenzophenone, diphenylmethane, and sulfur on distillation of

$$(C_6H_5)_2CHSSCH(C_6H_5)_2 \rightarrow (C_6H_5)_2CS + (C_6H_5)_2CH_2 + S$$

tetraphenyldimethyl disulfide.

6. Special methods

(*a*) *Action of carbon disulfide on imines and anils:*

$$[(CH_3)_2NC_6H_4]_2C{=}NH + CS_2 \rightarrow HSCN + [(CH_3)_2NC_6H_4]_2CS$$

$$[(CH_3)_2NC_6H_4]_2C{=}NC_6H_5 + CS_2 \rightarrow C_6H_5NCS + [(CH_3)_2NC_6H_4]_2CS$$

Fehrmann (59) reported that Michler's thioketone could be formed by warming the corresponding anil or imine with carbon disulfide. Phenyl isothiocyanate or thiocyanic acid was obtained as the other product.

(*b*) *Action of phosphorus pentasulfide on ketones:* Treatment of diaryl ketones with phosphorus pentasulfide has not been generally successful. Gattermann and Schulze (75) pointed out that thiobenzophenone could not be prepared by this method, and made the general statement that it was a poor method of preparing diaryl thiones. However, the preparation of *p,p'*-tetramethyldiaminodiphenyl thione by treating Michler's ketone with phosphorus pentasulfide has been patented (German patent 39,074; see Schönberg *et al.* (190)).

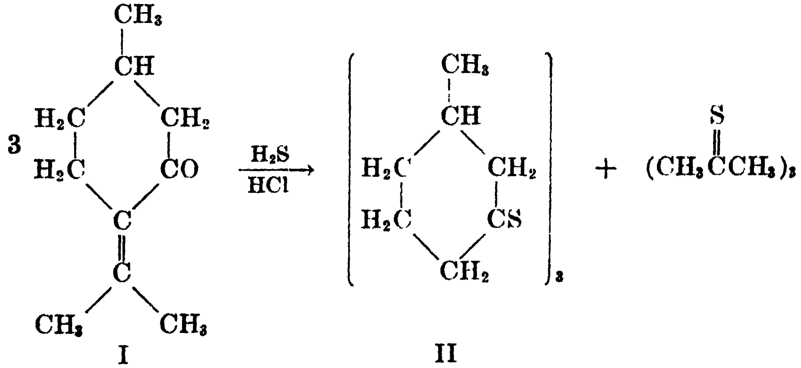
(*c*) *Action of thioacetoacetic ester on benzophenone:* Mitra (137) reported the preparation of a blue oil, boiling at 175°C. at 10 mm. pressure, by treating benzophenone with ethyl thioacetoacetate and dry hydrogen chloride. This compound was not crystallized, but it analyzed correctly for $C_{13}H_{10}S$ and the molecular weight was 198. The yield in this reaction was 27 per cent of the redistilled oil.

F. HOMOCYCLIC THIONES

A few of the simple homocyclic thiones have been prepared, and some of the thiones of the terpene series (thiocamphor, etc.) have been investigated. Two authors, Ray (160) and Sen (195), prepared thiocamphor by the hydrogen sulfide–hydrogen chloride method, and obtained a red crystalline compound which analyzed correctly for $C_{10}H_{16}S$, gave the oxime, phenylhydrazone, and semicarbazone of camphor, and melted at 145°C. In the earlier literature, however, three other reports, by Houben and Doscher (96), Rimini (164), and Wuyts (229), describe the preparation of a red crystalline compound which also analyzed correctly for thiocamphor, gave camphor derivatives, and melted at 119°C. These authors prepared the compounds by pyrolysis of the disulfides, a reaction which involves rearrangement. It is difficult to choose the correct constants for thiocamphor from the available data.

1. *Action of hydrogen sulfide on ketones*

This method has been used to prepare most of the known homocyclic thiones. Fromm (66) noted that cyclopentanone, cyclohexanone, and *p*-methylcyclohexanone all give well-crystallized trithiones in good yield upon treatment with hydrogen sulfide and hydrogen chloride in cold alcohol. However, when pulegone (I) was treated in a similar manner, a compound, $C_{21}H_{48}S_3$, which is probably trithio-*m*-methylcyclohexanone (II), was obtained. Trithioacetone was not isolated, but was identified by its characteristic odor.



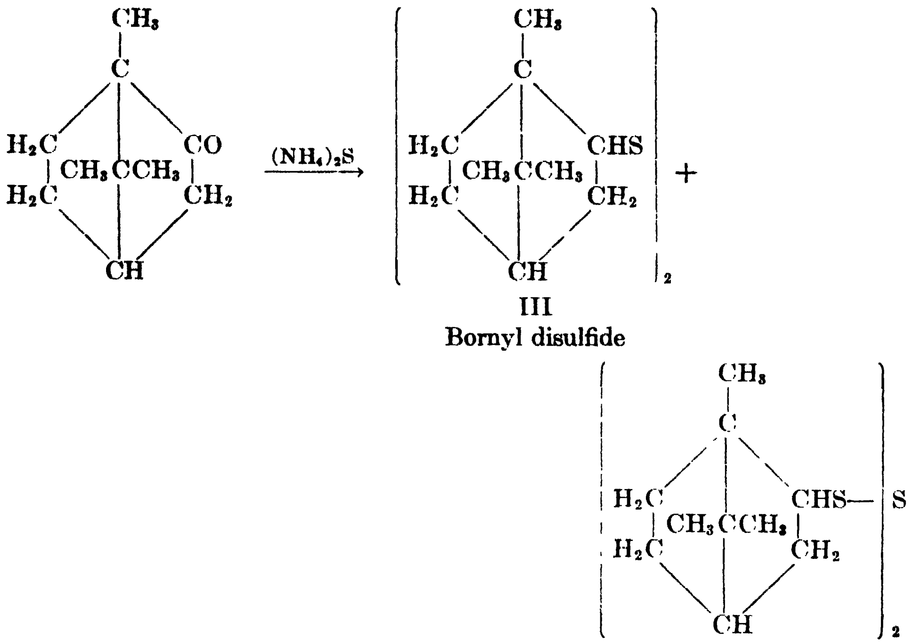
I
Pulegone

II

Sen (196) prepared the monomeric thiocyclopentanone and thiocyclohexanone by passing hydrogen sulfide and hydrogen chloride into a cold alcohol solution of the respective ketone for 1½ hr. At this point deep red solutions were obtained, which were distilled in vacuum. The resulting red oils gave the expected semicarbazones and phenylhydrazones. If these oils were further treated with hydrogen chloride in cold alcohol, they could be converted to the trithiones, which were identical with those prepared by Fromm. Molecular-weight determinations of the monomers in benzene indicated partial association. Ray (160) also reported the preparation of monomeric and trimeric thiocyclohexanone from cyclohexanone and hydrogen sulfide in cold alcoholic hydrogen chloride solution. Sen (195) reported a yield of 47 per cent of the purified thiocamphor by this method, and also prepared thiofenchone from fenchone (197) similarly.

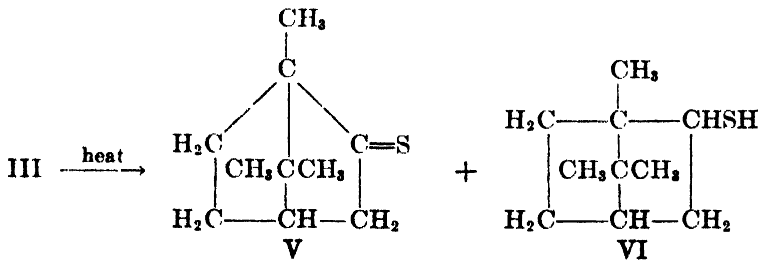
2. Pyrolysis of disulfides and mercaptals

This method has been used to prepare thiocamphor and thiofenchone. Wuyts (229) obtained bornyl disulfide (III) and bornyl trisulfide (IV) when he treated camphor with ammonium sulfide.



III
Bornyl disulfide

IV
Bornyl trisulfide

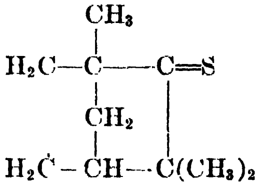


V

VI

$$\mathrm{IV} \xrightarrow{\text{heat}} \mathrm{V} + \mathrm{VI} + \mathrm{S}$$

III gave thiocamphor (V) and thioborneol (VI) on heating, while IV gave V, VI, and sulfur on heating. Houben and Doscher (96) prepared bornyl disulfide (III) by oxidizing thioborneol (VI) with chromium trioxide. Pyrolysis of III gave V and VI. Rimini (164) prepared both thiocamphor and thiofenchone (VII) by pyrolysis of the disulfides.

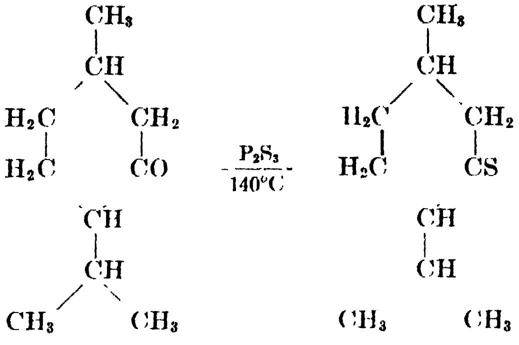


VII

Schönberg and Schutz (184, 187) heated the dibenzylmercaptal of fluorenone, and obtained a highly colored compound, presumably thiofluorenone, but did not record the properties of this thione.

3. Action of phosphorus trisulfide on ketones

Speranski (202) has investigated the effect of phosphorus trisulfide on various homocyclic ketones. When menthone (VIII) was heated with phosphorus trisulfide, thiomenthone (IX) was obtained as a high-boiling red oil. The molecular weight of this compound indicates that it is the monomer. Camphor and methylcyclohexanone also reacted with phosphorus trisulfide to yield the corresponding thiones.

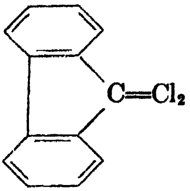


VIII
Menthone

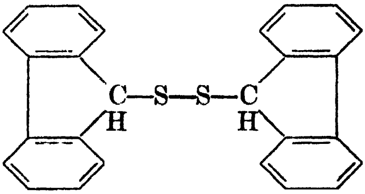
IX
Thiomenthone

4. Special methods: reaction of halides with metal sulfides

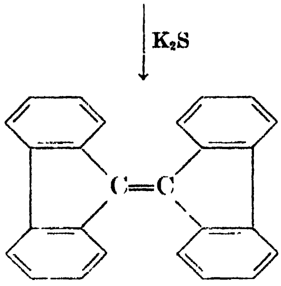
Smedley (201a) attempted to prepare thiofluorenone by treating 9,9-dichlorofluorene (X) with alcoholic potassium bisulfide or potassium sulfide. The reaction with potassium bisulfide yielded a white crystalline compound, melting at 167°C., which was thought to be the dimeric thiofluorenone, but was later shown by Bergmann and Hervey (30) to be the disulfide (XI). Treatment of X with potassium sulfide gave bis-diphenyleneëthylene (XII), red plates, m.p. 187–188°C. Bergmann and Hervey (30) were able to prepare the dimer XIII, m. p. 232°C., by treating fluorenone with hydrogen sulfide and hydrogen chloride in cold alcohol. No monomeric thiofluorenone was obtained in either of the above reactions, or by treatment of the ketone with phosphorus pentasulfide.



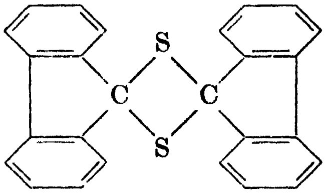
X



XI

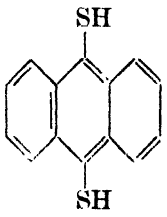


XII

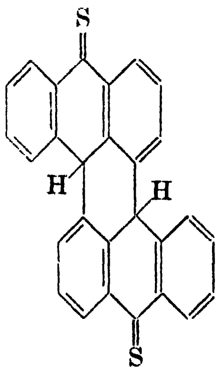


XIII

Heilbron and Heaton (86) attempted to prepare anthracene-9,10-dithiol (XIV) by treating 9,10-dibromoanthracene with sodium bisulfide in amyl alcohol. Instead they obtained a bright yellow, highly insoluble compound, melting at 320°C., to which they assigned structure XV and the name "dithioheptacylene." In a later paper, Cooke, Heilbron, and Walker (51) noted that



XIV



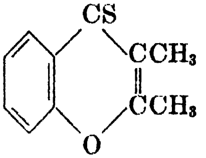
XV

9,10-dibromoanthracene was completely converted to XV by treatment with excess sodium sulfide for 2 hr. in an autoclave at 150°C. The structure XV has not been proven.

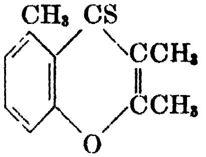
G. HETEROCYCLIC THIONES

1. *Effect of phosphorus pentasulfide on ketones*

The heterocyclic thiones are relatively stable, high-melting compounds, which are easily prepared by several methods. By far the largest number of heterocyclic thiones have been prepared by fusing phosphorus pentasulfide with the required ketone, and extracting the cooled, pulverized mass with a solvent, such as benzene or acetone. The solvent is then removed and the residue recrystallized from an appropriate solvent, such as alcohol. The yields on this reaction are generally good. Thus, Simonis and Rosenberg (201) obtained 2,3-dimethylthiochromone (I) in 70 per cent yield, and 2,3,5-trimethylthiochromone (II) in 100 per cent yield. The reaction is sometimes complicated by the conversion of the thione to an ethylene derivative by loss of sulfur.

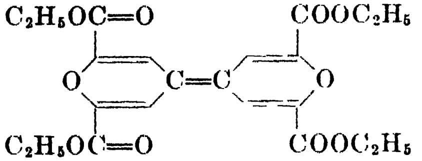


I

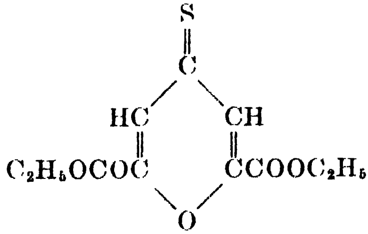


II

Arndt and Nachtwey (3) boiled phosphorus pentasulfide with diethyl chelidonate in benzene, and obtained the tetracarbethoxydipyrylene (III) instead of the expected diethyl 4-thiochelidonate (IV). They were able to obtain the desired compound by running the reaction in the presence of mercuric chloride, which precipitated as an insoluble complex with the thione.

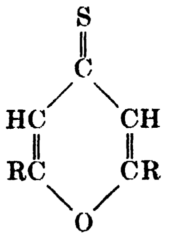


III

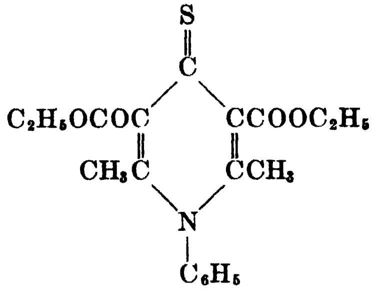


IV

However, most of the heterocyclic thiones are sufficiently stable to be prepared by fusing with phosphorus pentasulfide. Arndt, Scholz, and Nachtwey (5) prepared 4-thiopyrone (V), 2,6-dimethyl-4-thiopyrone (VI), and 2,6-diphenyl-4-thiopyrone (VII) by fusing the ketone with twice the calculated quantity of phosphorus pentasulfide for ½ to 1 hr., followed by extraction with benzene and recrystallization of the product from petroleum ether. This method has received its largest application with those heterocyclic ketones containing

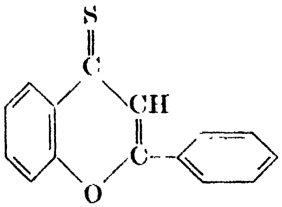


V: R = H
VI: R = CH_3
VII: R = C_6H_5



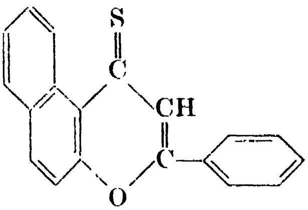
VIII

oxygen or sulfur in the ring. In this way, Schönberg and Nickel (181) synthesized 4-thioflavone (IX) and α naphtho-4-thioflavone (X); Simonis and Elias (199) prepared 2,3-dimethyl-1,4-dithiochromone (XI); and Arndt, Nachtwey, and Pusch (4) obtained 1,4-dithioflavone (XII).



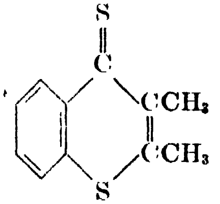
IX

4-Thioflavone



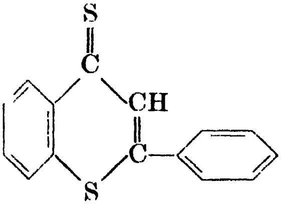
X

α-Naphtho-4-thioflavone



XI

2,3-Dimethyldithiochromone

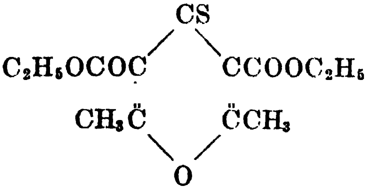


XII

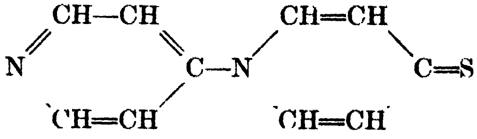
1,4-Dithioflavone

This method can be used with the nitrogen heterocycles, but apparently other methods are more efficient. Guthzeit and Epstein (83) prepared diethyl *N*-phenyl-2,6-dimethyl-4-thiopyridone-3,5-dicarboxylate (VIII) by fusing the ketone with phosphorus pentasulfide, and also by heating diethyl 2,6-dimethyl-

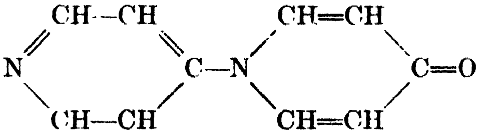
4-thiopyrone-3,5-dicarboxylate (XIII) with aniline in acetic acid. Arndt (2) prepared *N*-4-pyridyl-4-thiopyridone (XIV) by fusing the anhydride of 4-hydroxypyridine with phosphorus pentasulfide, and offers this compound as evidence for the keto form (A) of the 4-hydroxypyridine anhydride, rather than the ether form (B).



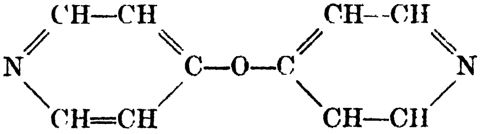
XIII



XIV



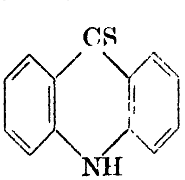
A



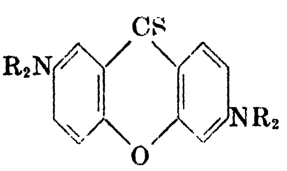
B

2. Oxidation of methylene and ethylene derivatives with sulfur

Several basic methylene derivatives have been converted to the thiones by simply heating the compound with sulfur. Edinger and Arnold (56, 101) obtained thioacridone (XV) by heating acridine with sulfur at 190–195°C. for 4 hr., and recrystallizing the product from alcohol. Rodd and Stocks (165) patented a process for the preparation of 3,7-tetraalkyldiaminoxanthones, which depends on the formation of the xanthiones (XVI) by heating the 3,7-tetraalkyldiaminoxanthenes with sulfur in boiling xylene for 24 hr. The xanthiones may be converted to the xanthones by boiling with hydrochloric acid.

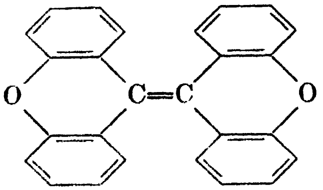


XV
Thioacridone

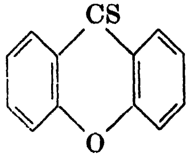


XVI

Schönberg (172) originally noted that dixanthylene (XVII) was converted to xanthione (XVIII) by fusion with sulfur. Bergmann and Engel (29) assume that this reaction takes place by addition of two sulfur atoms to the double bond,

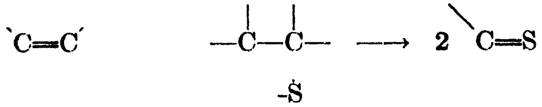


XVII
Dixanthylene



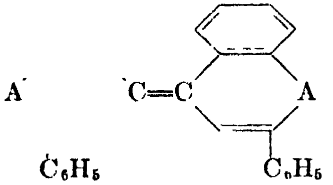
XVIII
Xanthione

to form the hypothetical ring disulfide, which then dissociates to two molecules of the thione. However, the tetraarylethylenes do not undergo this reaction.

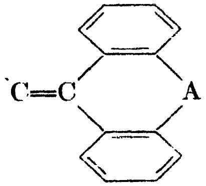


$$\diagdown C{=}C\diagup \qquad -\overset{|}{C}-\overset{|}{C}- \longrightarrow 2\ \diagdown C{=}S$$
$$\text{-}\dot{S}$$

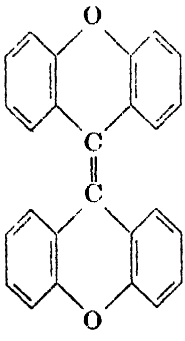
Schönberg and Askar (175) investigated the reaction of sulfur with ethylenes rather extensively, and found that a variety of heterocyclic ethylene compounds underwent this reaction. Diflavylene (XIX), dithioflavylene (XX), dithioxanthylene (XXI), and di-*N*-methylacridylene (XXII), all react with sulfur at about 280°C., like dixanthylene, to give the corresponding thiones. On the other hand, tetraarylethylenes like tetraphenylethylene, tetraanisylethylene, tetrabiphenylethylene, and tetra-*p*-dimethylaminophenylethylene do not react.



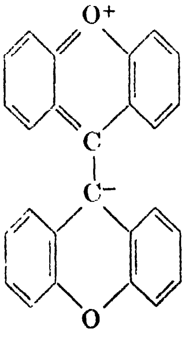
XIX: A = O
XX: A = S



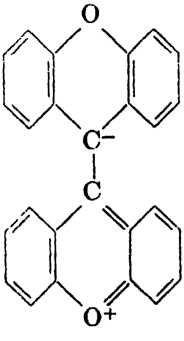
XXI: A = S
XXII: A = NCH_3



A

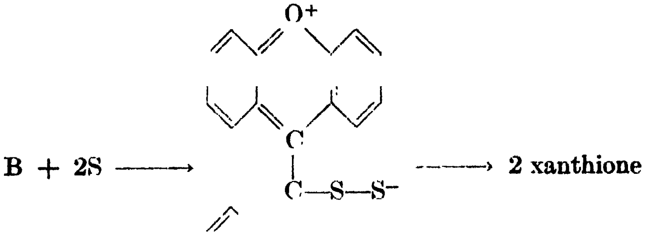


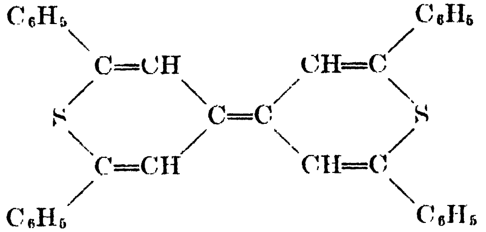
B,B′



C,C′

Schönberg and Askar therefore conclude that the reaction is due to the heterocyclic structure, and may be explained on the basis of resonance hybrids. For instance, xanthylene may exist in five different resonance structures A, B, B′, C, and C′, in which the prime letters indicate quinoid structure in the alternate aromatic ring. Sulfur may then add to the unshared electrons on the negative carbon and the resulting disulfide could dissociate to two molecules of xanthione. The failure of 2,6,2′,6′-tetraphenyldithiopyrylene (XXIII) to form the thiopyrone when heated with sulfur is attributed to the fact that the reverse reaction



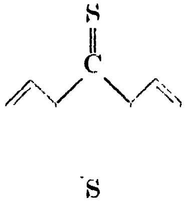


XXIII

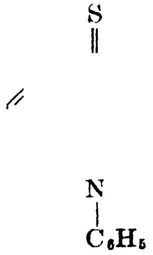
(conversion of the thiopyrone to the dithiopyrylene) takes place at low temperature.

3. *Action of thioacetic acid on keto chlorides*

The reaction of thioacetic acid with the keto chlorides of diaryl ketones has been mentioned previously (page 27). Schönberg, Schutz, and Nickel (190)



XXIV
Thioxanthione



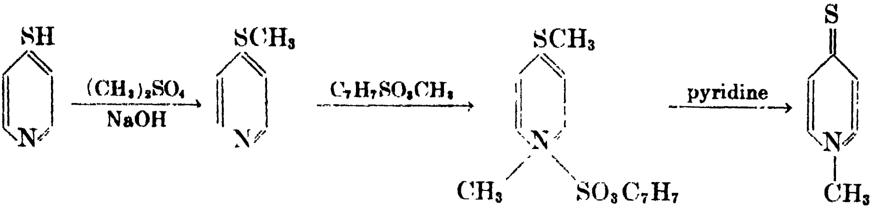
XXV
N-Phenylacridone

found this reaction to be equally valuable in the heterocyclic series, and in this manner were able to prepare xanthione (XVIII), thioxanthione (XXIV), and *N*-phenylthioacridone (XXV). The properties of thioxanthione prepared in this way differ from those of the thioxanthione prepared by fusion of the ketone with phosphorus pentasulfide, however. Meyer and Szanecki (132) prepared both xanthione and thioxanthione by fusion of the ketones with phosphorus pentasulfide. The properties of xanthione are the same when it is prepared by either method (red needles, m.p. 155–156°C.), but Schönberg and coworkers report thioxanthione to be greenish black plates, melting at 168°C. This compound is also obtained from dithioxanthylene and sulfur. Meyer and Szanecki report the compound to be olive-green, and to melt at 215°C. The properties of thioxanthione (XXIV) are therefore indefinite.

4. Special methods

(a) From thioethers of heterocyclic nitrogen bases

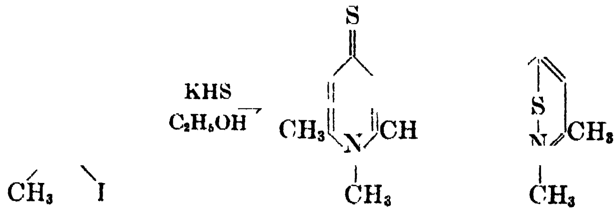
Kendall (103) has patented a method for the synthesis of *N*-alkylated heterocyclic thiones from the mercaptans, which involves heating the quaternary salt of the thioether in a weak organic base, such as pyridine. In this manner *N*-methyl-4-thiopyridone (XXVI) was synthesized by treating 4-mercaptopyridine with methyl sulfate and alkali, and converting the resulting thioether to the quaternary methyl tosylate with methyl toluenesulfonate. Boiling this salt in pyridine resulted in the formation of *N*-methyl-4-thiopyridone.



XXVI

(b) Action of halogenated nitrogen heterocycles with metal bisulfides or thiosulfates

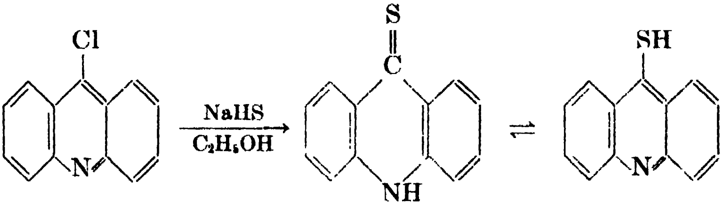
The γ-halogenated pyridines and acridines have been found to react with metal bisulfides to give the thiopyridones and thioacridones. By this means



XXVIII XXVII

Michaelis and Holken (134) were able to prepare *N*-methyl-4-thiolutidone (XXVII) by treating 4-chlorolutidine methiodide (XXVIII) with potassium bisulfide. It was suggested that this compound exists in the tautomeric thione (A) and thiol salt (B) forms because, although it gave several thione reactions, treatment with methyl iodide gave the thiomethyl ether methiodide.

A series of thioacridones has been prepared by Cherntsov (47) by treating 9-chloroacridine (XXIX) or its derivatives with sodium bisulfide in alcohol, and



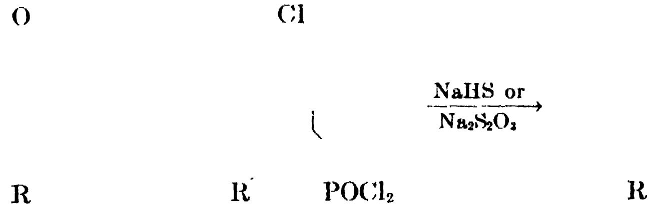
A B

XXIX XV

9-Chloroacridine

yields of over 90 per cent in all cases were reported. The compounds prepared were chloro, methyl, and methoxy derivatives of thioacridone (XV). These compounds also exist in the thione–thiol (A–B) tautomeric forms.

Gleu and Schaarschmidt (77) used a variation of this method to synthesize several *N*-substituted thioacridones, after trying several alternate methods. These authors found that alkylation of thioacridones gave exclusively the *S*-alkyl derivatives, which did not isomerize to the desired *N*-alkyl compounds on heating. Heating the appropriate *N*,*N'*-disubstituted acridylenes with sulfur gave the desired compounds, but the most efficient preparation utilized the 9-chloroacridinium dichlorophosphates as intermediates. When *N*-substituted

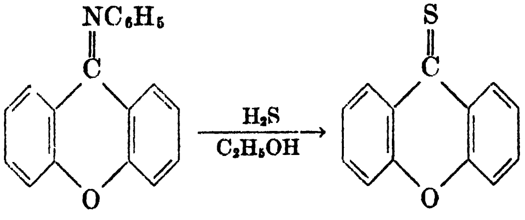


XXX XXXI XXXII

acridones (XXX) are treated with phosphorus oxychloride, the quaternary 9-chloroacridinium dichlorophosphates (XXXI) result. When these salts are reacted with sodium bisulfide or sodium thiosulfate, the desired thiones (XXXII) are produced in good yield. Gleu and Schaarschmidt reported that the reaction with sodium thiosulfate was almost quantitative even in excess mineral acid, indicating that it was faster than the decomposition of thiosulfuric acid. Sodium thiosulfate does not react readily with the non-quaternary salts of 9-chloroacridine, however. This method was used to prepare the *N*-methyl-, *N*-ethyl-, and *N*-phenyl-thioacridones.

(c) Action of hydrogen sulfide on ketone derivatives

When the anil of xanthone (XXXIII), prepared by heating *o,o'*-dihydroxybenzophenone with aniline, was dissolved in alcohol, and the hot solution saturated with hydrogen sulfide for 24 hr., xanthione (XVIII) was obtained (Graebe and Roder (78)). No yield was reported for this reaction.



XXXIII XVIII

(d) Pyrolysis of mercaptals and thioethers

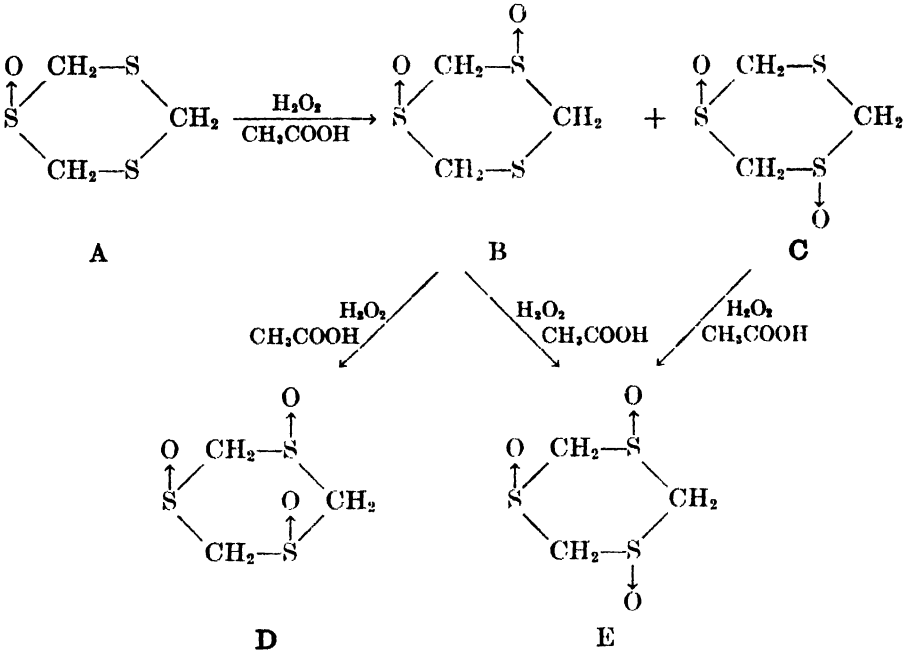
Schönberg and Schutz (184, 187) found that the mercaptals of xanthone and thioxanthone were most easily converted to the thiones by heat. Schönberg, Schutz, Bruckner, and Peters (188) found that dixanthyl thioether was converted at 185°C. to xanthene and xanthione. The yield in this reaction is not high.

V. PHYSICAL PROPERTIES AND MOLECULAR STRUCTURE

A. ISOMERS OF THE TRIMETHYLENE TRISULFIDE RING

The problem of *cis* and *trans* isomers has been difficult to resolve in the case of the trimethylene trisulfide ring, owing to the occurrence of polymorphism, eutectic mixtures, and trithioformaldehyde polymers. For a time, it was assumed that there were two isomers of *s*-trithiane itself. As previously noted (page 5), Baumann and Fromm (20) had separated a variety of compounds from a crude preparation of *s*-trithiane, which included polymers and complex oxygen- and sulfur-containing compounds. Hinsberg (87, 88) reduced trimethylene trisulfoxide with concentrated hydrogen iodide, and obtained a compound melting at 247°C. which he claimed to be a β-form of *s*-trithiane. (The α-form melts at 216°C.) It was possible to reconvert this compound to the α-form by recrystallization. Hinsberg attributed the existence of a second isomer of *s*-trithiane to the spacial characteristics of the sulfur atom (90). Fromm and Soffner (71) investigated this problem, and concluded that Hinsberg's β-form was actually a cyclic methylene sulfur compound, $(CH_2S)_x$, in which x was greater than 3. Hinsberg, however (92), claimed that his compound gave the same trisulfone, $(CH_2SO_2)_3$, upon complete oxidation with potassium permanganate, as did *s*-trithiane, and that therefore it must retain the same ring structure as *s*-trithiane. This is not very conclusive, since trithiane trisulfone decomposes without melting at about 320°C., making its identity with other sulfones difficult to prove.

Fromm and Soffner's criticism was beautifully confirmed by Bell and Bennett (27), who were able to separate all of the sulfoxides which would theoretically exist for a planar trimethylene trisulfide ring. Oxidation of *s*-trithiane with hydrogen peroxide in acetone yielded only one monoxide, A. Further oxidation with the calculated amount of hydrogen peroxide in acetic acid gave two disulfoxides, B and C, which could be separated by fractional crystallization from water. Since these oxides also decompose at high temperatures without melting, their non-identity was demonstrated by their crystalline properties and solubility. Compound C, upon further oxidation with hydrogen peroxide in acetic acid, yielded only one trisulfoxide, E. The *trans* configuration was therefore assigned to C, and the *cis-trans* configuration to E. This agrees with their solubilities and stabilities. Compound B, upon further oxidation, yielded two trisulfoxides, which were separated by fractional crystallization. One of these was identical with E, and the other, D, was assigned the *cis-cis* configuration. This would indicate that B has the *cis* configuration. The existence of these various *cis-* and *trans*-sulfoxides proves that *s*-trithiane exists in a simple planar ring structure.

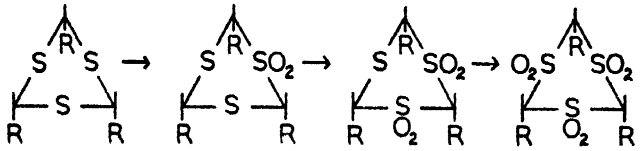


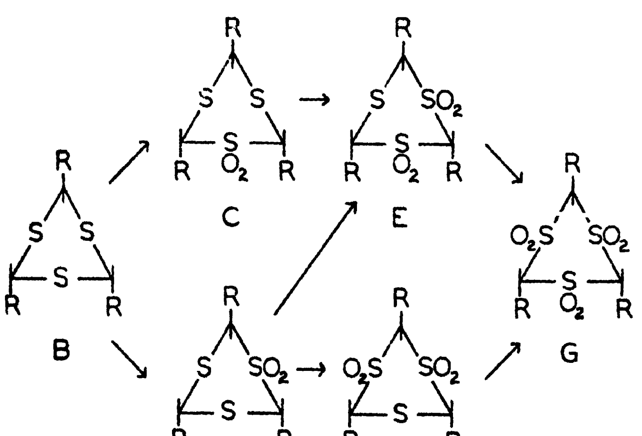
1. Trithioacetaldehyde

Trithioacetaldehyde is the only 2,4,6-trialkyltrithiane which has been investigated in regard to *cis* and *trans* forms. Klinger (107) originally proposed the cyclic structure for trithioacetaldehyde, and separated the two isomers, α-trithioacetaldehyde, m.p. 101°C., and β-trithioacetaldehyde, m.p. 125–126°C.

Baumann and Fromm (15) carried out an extensive investigation of the *cis* and *trans* isomers of both trithioacetaldehyde and trithiobenzaldehyde. By treating acetaldehyde with hydrogen sulfide and hydrogen chloride in cold alcohol, they were able to isolate the α- and β-forms, and a γ-form, m.p. 85–95°C., which they later (17) showed to be a mixture of the two isomers. Suyver (215) explored the eutectic mixtures of α- and β-trithioacetaldehydes, and found that a mixture of 60 per cent α-form and 40 per cent β-form melts rather sharply at 75-76°C. This is undoubtedly the γ-form, which Mann and Pope (125) claimed was formed when α,α′-dichlorodiethyl sulfide was treated with silver sulfide, hydrogen sulfide, silver oxide, or sodium hydroxide (page 9). Fromm and Engler (67) prepared the trisulfoxides of α-, β-, and γ-trithioacetaldehydes by oxidation with 30 per cent hydrogen peroxide in glacial acetic acid, and obtained an α-trisulfoxide melting at 184°C. and a β-trisulfoxide melting at 153°C. The trisulfoxide from the γ-form was identical with that from the α-form. This work is not conclusive, however, since there should theoretically be two trisulfoxides for each form.

Baumann and Fromm (15) had concluded that the more stable, higher-melting β-forms of trithioacetaldehyde and trithiobenzaldehyde were the *trans* isomers, by analogy with the *trans*-hexahydrophthalic acid. These authors realized that the sulfoxides would give too many isomers to be useful for positively proving which of the two forms was *cis*, and which *trans*, and therefore proposed to use the mono-, di-, and tri-sulfones (17). Thus the *cis* form of a 2,4,6-trisubstituted trithiane (A) would theoretically yield only one mono-





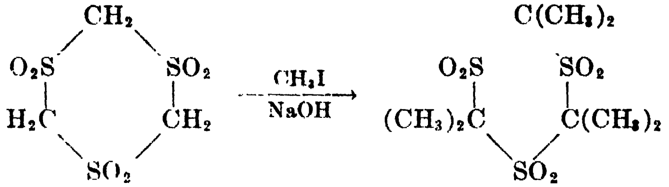
sulfone, one disulfone, and one trisulfone, while the *cis–trans* form (B) would yield two monosulfones, depending on whether the sulfur atom between the two *cis* substituents was oxidized (C) or whether either of the other two sulfur atoms were attacked (D). The monosulfone C would then yield only one disulfone (E), while the monosulfone D would yield two disulfones (E and F), and both E and F would yield the same trisulfone (G). Baumann and Fromm were unable to carry out all of these reactions, but found that direct oxidation of α- and β-trithioacetaldehydes to the trisulfones with potassium permanganate in sulfuric acid yielded products melting above 300°C. which were apparently the same! This was later proved to be the case by Lonnitz (122), who prepared derivatives of both trisulfones which were identical with one another. Baumann (12) was able to prepare the disulfones by permanganate oxidation of the α- and β-trithioacetaldehydes, and again found only one disulfone, melting at 283–284°C., instead of three, as called for by the theory. It was therefore assumed that rearrangement had occurred on oxidation.

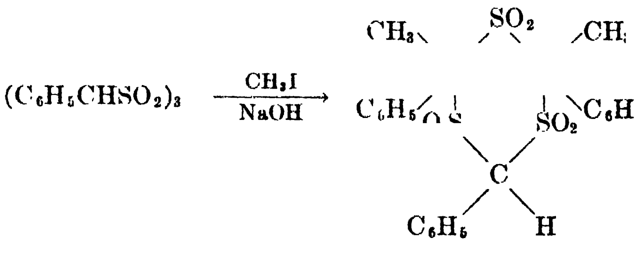
Chattaway and Kellett (46) investigated the monosulfoxides and monosulfones of α- and β-trithioacetaldehydes, and found that oxidation of β-trithioacetaldehyde (m.p. 126°C.) with hydrogen peroxide gave one monosulfoxide, which on oxidation with potassium permanganate in dilute magnesium sulfate solution gave one monosulfone, m.p. 190°C. This sulfone could not be reduced to the original β-trithioacetaldehyde, but the sulfoxide was so reduced by zinc and hydrochloric acid. Oxidation of the α-isomer (m.p. 101°C.) in a similar manner yielded two monosulfones, one melting at 157°C., and the other at 115–116°C. Mixed melting points proved these three monosulfones to be different. Since the α-isomer yielded two monosulfones, and the β-isomer only one, it was concluded that the lower-melting, more soluble α-compound had the *cis–trans* configuration (B, $R = CH_3$) and that the higher-melting, less soluble β-compound was the *cis* compound (A, $R = CH_3$). This is contrary to the usual behavior of *cis* and *trans* isomers. The conversion of Chattaway and Kellett's monosulfones to the corresponding disulfones has not been reported. Of the trithioacetaldehyde isomers, the γ-form has fairly definitely been proved to be a mixture of the α- and β-forms, but which of the two pure forms is *cis–trans* and which *cis–cis* may still be open to question.

2. Trithiobenzaldehyde and derivatives

The problem of the isomeric *cis–cis* and *cis–trans* trithiobenzaldehydes parallels very closely the same question in the thioacetaldehyde group. Baumann and Fromm (15) originally separated three compounds, α-trithiobenzaldehyde, m.p. 166–167°C., β-trithiobenzaldehyde, m.p. 225–226°C., and γ-trithiobenzaldehyde, m.p. 83–85°C. By analogy with the trithioacetaldehydes, they concluded that the γ-form was a mixture of the α- and β-forms. Suyver (215) later confirmed this conclusion, and studied the solubilities of the α- and β-forms. It was found that the α-trithiobenzaldehyde was much more soluble than the β-isomer, e.g., fifty times more soluble in chloroform, and sixty times more soluble in benzene.

Baumann and Fromm prepared a series of substituted trithiobenzaldehydes (18, 19, 21) and found two isomers for each of the compounds they prepared. Kopp (111) and Worner (228) also prepared substituted trithiobenzaldehydes, and although they were sometimes only able to prepare one of the two possible isomers, in no case were more than two isomers found. Hinsberg (89, 91) claimed to have prepared a third modification of trithiobenzaldehyde by oxidation of the β-isomer to the tetroxide, and reduction of this oxide with hydrogen iodide, but Fromm and Schultis (70) were able to refute this claim by demonstrating that rearrangement occurs very readily on oxidation of the 2,4,6-triphenyltrithiane isomers. Thus the same trisulfoxide was obtained when either α- or β-trithiobenzaldehyde was oxidized with hydrogen peroxide in acetic acid. Reduction of this trisulfoxide yielded only β-trithiobenzaldehyde, the more stable form. Fromm and Schultis believed this to be the *cis–trans* form, because of its stability, high melting point, and low solubility, and because it exhibited hindrance when the trisulfone was treated with methyl iodide in sodium hydroxide solution. Ordinarily, when a trimethylene trisulfone is treated in this manner, all of the hydrogens on the methylene groups are replaced by methyl groups. In this way, Baumann and Camps (13) obtained the trisulfone of trithioacetone by treating trimethylene trisulfone with methyl iodide in sodium hydroxide. However, if the trisulfone of trithiobenzaldehyde is treated in this manner, only two methyl groups are added. Fromm and Schultis explain this on the assumption that one of the methylene hydrogens is less reactive because it is between two phenyl groups, thus indicating the *cis–trans* structure for the trisulfone and trisulfoxides of trithiobenzaldehyde, and consequently, the same structure for the β-trithiobenzaldehyde itself.





B. COLOR OF MONOMERIC THIOCARBONYL COMPOUNDS

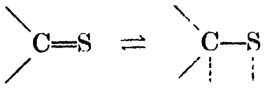
With few exceptions, all of the monomeric thiones are colored compounds. This property is useful in determining the point at which the trimers dissociate.

For instance, trithioacetophenone gives a blue solution in boiling xylene; the color gradually fades as the solution is cooled and association takes place. In the monomeric thiones, the color varies with the temperature. Cherntsov (47) noted an increase in the color intensity of thioacridones when they were heated above 110–120°C. Schönberg (174) mentioned the fact that some of the substituted diaryl thiones and heterocyclic thiones changed color on cooling to very low temperatures. Di-*p*-anisylthione changes from blue to violet on cooling in an acetone and dry ice mixture. Straus and Zeime (214) noted the influence of auxochrome groups on the thiones. Tetramethyldiaminothiobenzophenone is orange-red, while thiobenzophenone itself is deep blue in color. Staudinger and Siegvart (212) also commented on this variation of color, but showed that it did not influence the reactivity of the thione group. Violet thiobenzophenone, blue *p,p'*-dimethoxythiobenzophenone, and red *p,p'*-tetramethyldiaminothiobenzophenone all react with equal speed with diphenyldiazomethane.

1. Absorption spectra

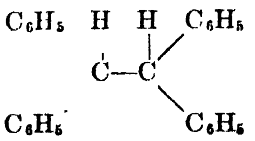
The absorption curves of various thiones have been measured. Bost and Cosby (39) found absorption bands at about 5900 Å. for phenyldiphenylthione, phenyl-*p*-tolylthione, and phenyl-α-naphthylthione. Sen (197) found a band at 4950 Å. for thiofenchone. Burawoy (41, 42) compared the absorption spectra of the chromophoric C=NH, C=O, and C=S groups, and found that extinction increased in that order, and also noted that the absorption bands were shifted toward the red in the same order. On the basis of the optical properties of the thiones, Burawoy proposed that they may exist in a free-radical form to a small extent. Donle and Volkert (53) also found a significant difference in the ultraviolet-absorption curves of compounds containing the carbonyl and thiocarbonyl groups, a result which showed a difference in the structure of the two groups.

The color characteristics associated with the thiocarbonyl group are comparable to the color properties of free radicals. Bergmann, Magat, and Wagenberg (31) noted the similarity in the color change when the methoxy or dimethylamino groups were introduced into diaryl ketones or into hexarylethanes, and suggested that the monomeric thione group may be represented as a tautomeric thione–free-radical arrangement. This is borne out by other observations. In many chemical reactions, diaryl thiones behave like triarylmethyls. For example, both triphenylmethyl and thiobenzophenone take up oxygen in the air to form unstable peroxides.

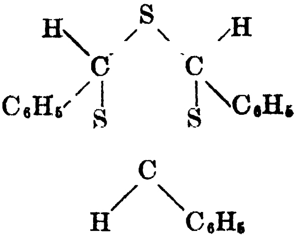


2. Tendency to polymerize

The suggestion that the monomeric thiones may exist as free radicals caused Schönberg (173) to compare the dissociation tendencies of the polymeric thiones with the dissociation tendencies of corresponding members of the ethane series. Tetraphenylethane (I) and 2,4,6-triphenyltrithiane (II) are stable, but if the hydrogens are replaced by phenyl groups, then the tendency to dissociate is



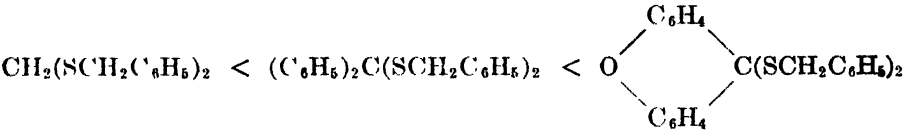
I



II

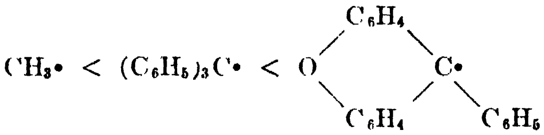
greatly increased. Schönberg made the generalized statement that the same substituents which increase the stability of free radicals will increase the stability of the thione monomers.

Parallel observations were made by Schönberg and Schutz (184, 187) on the pyrolysis of mercaptals. In the dibenzylmercaptal series, the tendency to decompose on heating increases with the size of the methylene substituents, and this tendency parallels the dissociation of substituted ethanes. The ease of pyrolysis may be represented by the following series:



$$CH_2(SCH_2C_6H_5)_2 < (C_6H_5)_2C(SCH_2C_6H_5)_2 < O{<}^{C_6H_4}_{C_6H_4}{>}C(SCH_2C_6H_5)_2$$

in which the xanthone derivative decomposes most readily. The stability of the free radicals may be represented by the series:



$$CH_3\bullet < (C_6H_5)_3C\bullet < O{<}^{C_6H_4}_{C_6H_4}{>}C\bullet-C_6H_5$$

in which phenylxanthyl is the most stable.

Schönberg, Rupp, and Gumlick (183) found evidence for the existence of free sulfur radicals in compounds other than the thiones, and they suggest the name "thiyl" for the free radicals of this type. It was found that diphenyl disulfide did not obey Beer's law in solution, and that it reacted with diazomethane and other reagents like a free radical.

$$C_6H_5SSC_6H_5 \rightleftharpoons 2C_6H_5S\bullet$$

C. OTHER PHYSICAL EVIDENCE OF MOLECULAR STRUCTURE

1. Dipole moment

Sidgwick (198) has reviewed the work on the dipole moment of the C═S group. The results of several groups of workers indicate that the moment of the C=S group is about 0.5×10^{-18} greater than that of the C=O group. Sidgwick assigned to them the values 3.0×10^{-18} and 2.5×10^{-18}, respectively. Donle and Volkert (53) measured the moments of dianisyl ketone and dianisyl thioketone, and obtained 3.8×10^{-18} for the former and 4.44×10^{-18} for the latter, a difference of 0.6×10^{-18}. These authors believed that this indicates a significant structural difference in the C=O and C=S groups, since a smaller moment would be expected for the C=S group. Hunter and Partington (97) corroborated these findings with the value of 2.95×10^{-18} for benzophenone and 3.4×10^{-18} for thiobenzophenone, an increase of $0\ 45 \times 10^{-18}$ for the latter.

2. Bond energies and interatomic distance

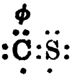
The bond energy for the C=O group is 152 kg.-cal., and that for the C=S group is 103 kg.-cal. (reference 117, page 1800; after Pauling). This rather large difference, indicating a much weaker bond, is not contradictory to the concept of the existence of a free-radical type of structure in the C=S group.

The interatomic distance is also in agreement with this concept. Use of the interatomic radii of Pauling and Huggins (117, page 1772) gives the value 1.61 Å. for the carbon-to-sulfur distance in C=S, and 1.26 Å. for the carbon-to-oxygen distance in C=O. These figures have been determined from measurements on carbon disulfide, thiourea, etc., and not on thiones.

Sufficient data are not available for any conclusions to be drawn about refractive indices or parachors for the thiones or thials.

3. Phosphorescence

Recently, Lewis and Kasha (120, 121) have made some interesting calculations based on phosphorescence and absorption of compounds in the triplet or biradical state. A typical example of this biradical state would be the free radical of thiobenzophenone ($\phi = C_6H_5$):



$$\phi:\underset{\cdot}{\overset{\phi}{\ddot{\mathrm{C}}}}:\underset{\cdot}{\ddot{\mathrm{S}}}:$$

Thiobenzophenone was used by these authors to demonstrate the identity of the phosphorescent and the triplet states. Thus they were able to calculate the triplet-state energy (E_t = kg.-cal.) for thiobenzophenone from both phosphorescence and absorption-spectrum data. It was shown that the abnormal colors of the monomeric thiones are due to absorption from the singlet to the triplet state.

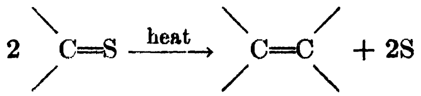
Lewis and Kasha (121) have also discussed the tendency of thiones to dimerize or trimerize, and have pointed out that, if E_{Dim} is written for the energy of association, then the dimer is thermodynamically stable when $E_{\mathrm{Dim}} > 2E_t$, where E_t stands for the triplet-state energy. Therefore, in all cases where E_t is small, dimerization might be expected, except where E_{Dim} is small, owing to steric hindrance or other effects, as in the case of di-*tert*-butyl thione. Similar conditions apply to the case of trimerization also.

VI. REACTIONS OF THIALS AND THIONES

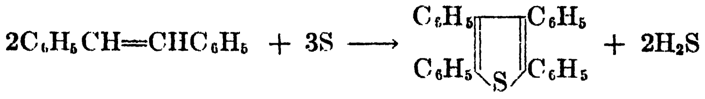
There is considerable physical evidence which indicates that the monomeric thiones exist partially in the biradical state, which frequently causes the C═S group to behave in chemical reactions in a different manner from the C═O group. In other reactions, however, it may behave as an analog of the carbonyl group.

A. EFFECT OF HEAT ON THIONES AND THIALS

The thiones and thials tend to lose sulfur under the influence of heat, to form ethylene derivatives. Although this reaction does not occur with all thiocarbonyl compounds, it seems to occur with both the monomers and trimers of those compounds which do react. The reaction has long been known. Fleischer reported the formation of stilbene and thionessal from the dry distillation of thiobenzaldehyde in 1866 (64). The thionessal was formed by the reaction of sulfur and stilbene at high temperatures. Barbaglia and Marquardt (10) obtained stilbene when benzaldehyde and sulfur were heated to 180°C. for 36 hr., and undoubtedly thiobenzaldehyde was an intermediate in this reaction.

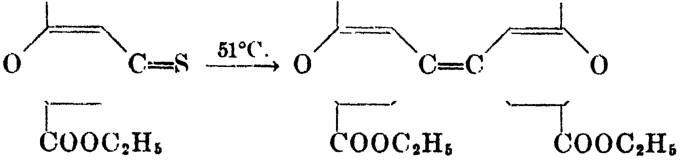


(1) $2C_6H_5CHS \longrightarrow C_6H_5CH{=}CHC_6H_5 + 2S$

(2)

$2C_6H_5CH{=}CHC_6H_5 + 3S \longrightarrow$ (tetraphenylthiophene ring: C_6H_5, C_6H_5, C_6H_5, C_6H_5, S) $+ 2H_2S$

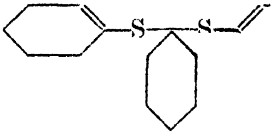
Kopp (110, 111) investigated the effect of heat on a series of aromatic thial trimers and found that the trimers of *o*-, *m*-, and *p*-hydroxythiobenzaldehydes were converted to the respective stilbene derivatives when they were heated above their melting points. *o*-Methoxythiobenzaldehyde was converted directly to the tetra-*o*-methoxyphenylthiophene on heating to 145°C., and no stilbene could be isolated from this reaction mixture. Wood and Bost (226) repeated Fleischer's work on the formation of thionessal by distillation of trithiobenzaldehyde. Later, these same authors (227) found that the ethylene derivative was obtained in 70 per cent yield when β-ethoxy-α-thionaphthaldehyde was heated to 300°C.

The conversion of heterocyclic thiones to the corresponding ethylene derivatives by heat has been investigated by Arndt and coworkers (3, 4, 5) and re-



viewed by Schönberg and Askar (176). Arndt and Nachtwey (3) observed that diethyl 4-thiochelidonate was converted at its melting point (51°C.) to the dipyrylene derivative (I). The remarkable ease of this conversion led Arndt, Scholz, and Nachtwey (5) to test thiopyrone, 2,6-dimethylthiopyrone, 2,6-diphenylthiopyrone, and xanthione in the same way. These authors found that the 2,6-diphenylthiopyrone was converted to the dipyrylene derivative above its melting point (173°C.), but that the others were not affected. Later Arndt, Nachtwey, and Pusch (4) found that 2,6-diphenyl-1,4-dithiopyrone was converted to the dithiopyrylene derivative at 145°C., but that 1,4-dithioflavone did not decompose on heating. It was therefore concluded that acidic groups, such as carbethoxy or phenyl, in the 2- and 6-positions were necessary for the conversion.

Behr (26) obtained some tetraphenylethylene upon heating thiobenzophenone, but the yield was very low. Fromm and Ziersch (72) found that thioacetylthioacetone dimer did not decompose on distillation. Fromm (66) found that when trithiocyclohexanone was heated above its melting point, hydrogen sulfide was evolved, and a compound, $C_{18}H_{28}S_2$, was obtained to which the following structure (II) was assigned.

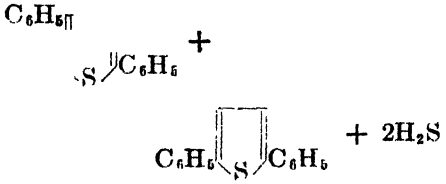


II

When trithioacetophenone was heated, several products were obtained (22). The trimer first dissociated to the monomer at about 145°C., and upon distillation this gave hydrogen sulfide, ethylbenzene, styrene, and both 2,4- and 2,5-diphenylthiophenes. No α,α'-dimethylstilbene was found. The various compounds are probably formed according to the following equations:

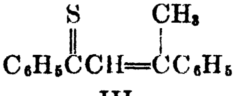
(1) $C_6H_5CSCH_3 \xrightarrow{\text{heat}} C_6H_5CH{=}CH_2 + S$

(2) $2C_6H_5CH{=}CH_2 + 3S \xrightarrow{\text{heat}}$



(3) $C_6H_5CH{=}CH_2 + H_2S \longrightarrow C_6H_5C_2H_5 + S$

Baumann and Fromm (22) also noted that heating "anhydroacetophenone disulfide" converted it to 2,4-diphenylthiophene. Probably thiodypnone (III)



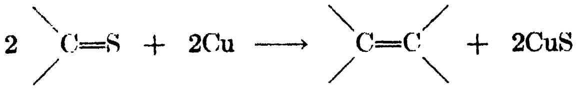
$$C_6H_5\overset{\overset{\displaystyle S}{\|}}{C}CH{=}\overset{\overset{\displaystyle CH_3}{|}}{C}C_6H_5$$

III
Thiodypnone

was an intermediate in this reaction, being converted to 2,4′-diphenylthiophene by loss of hydrogen. The reaction is facilitated by the use of copper chromite, a dehydrogenating catalyst (44).

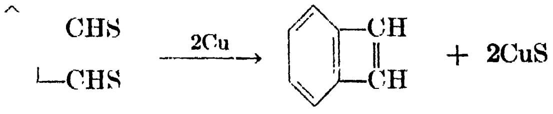
B. REACTION WITH METALS

The thiocarbonyl compounds are converted to ethylene derivatives with great ease when a metal which reacts with sulfur is present. The most commonly



$$2\ {>}C{=}S + 2Cu \longrightarrow {>}C{=}C{<} + 2CuS$$

used metal is copper or some form of activated copper, but iron, zinc, and nickel have been found effective also. Wislicenus (223) reported that heating thioacetone with copper powder gave copper sulfide, but the organic product was not identified. Later Klinger (105, 106) found that trithiobenzaldehyde was readily converted to stilbene when heated with copper powder, and suggested that this reaction might be used to prepare benzocyclobutadiene (IV). This synthesis has not been confirmed. Kopp (110) found that many of the substituted

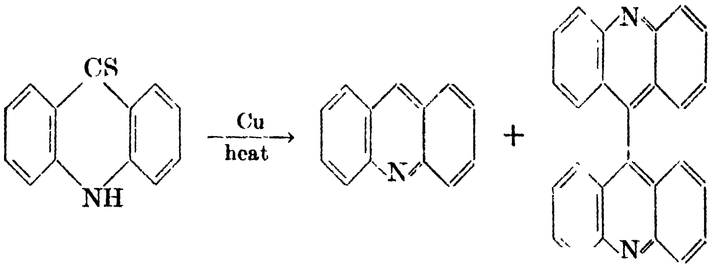


IV

thiobenzaldehydes were converted directly to the tetraarylthiophenes by heat, but if the compounds were heated with iron powder or zinc dust, the stilbene derivative was the chief product. Richtzentrain and von Hofe (163) converted trithiovanillin and trithioveratraldehyde to the corresponding ethylene derivatives by distillation with copper and iron powder, respectively. Even the hindered trithiomesitaldehyde was converted to hexamethylstilbene in 42 per cent yield by heating to 220–230°C. with copper bronze (73). The conditions for synthesizing symmetrical diarylethylenes in this manner were studied by Wood, Bacon, Meibohm, Throckmorton, and Turner (225). In these experiments, the appropriate substituted trithiobenzaldehyde was heated for ½ hour at 10–15°C. above its melting point with three to four times the calculated quantity of freshly reduced copper powder, and the substituted ethylene was isolated. The reaction was found to be applicable to unsubstituted, or alkoxy-substituted aryl thials. Trithiobenzaldehyde gave a 45 per cent yield of stilbene, and trithioveratraldehyde gave 25 per cent of the 3,4,3′,4′-tetramethoxystilbene, but hydroxy derivatives gave only traces of product and nitro derivatives did not react. Dithienylethylene was prepared by Steinkopf and Jakob (213) by heating trithiothienyl aldehyde with copper powder.

The reaction of copper powder with diaryl thiones to give the tetraarylethylenes has been found to take place with ease in most cases. Gattermann found the reaction to proceed with all of the alkoxy and halogenated diaryl thiones prepared by him (74). The reaction has been used as a means of identifying thiones (75, 219). Schönberg, Schutz, and Nickel (190) found that the reaction proceeded smoothly in boiling xylene. When thiobenzophenone was treated in this manner with copper bronze powder until the blue color of the solution disappeared—about 45 min.—tetraphenylethylene was obtained in 76 per cent yield. The alkoxy-substituted thiobenzophenones reacted somewhat less readily, and tetramethyldiaminothiobenzophenone gave very poor yields of the ethylene derivative.

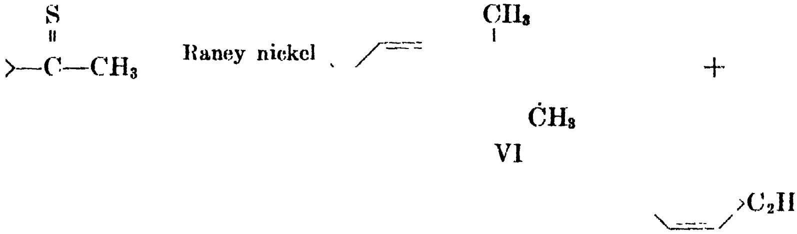
The reaction is not very useful in the heterocyclic series. Those heterocyclic thiones which are not converted to ethylene derivatives by heat are resistant to the reaction with copper (176). Schönberg (171) synthesized dixanthylene by heating xanthione with copper bronze, but when thioacridone was heated with copper powder, Lehmstedt and Hundertmark (118) obtained a mixture of reduction products containing 25 per cent of acridine and 59 per cent of 9,9′-diacridyl (V).



V

(25 per cent) (59 per cent)

Interest in stilbenes as synthetic sex hormones led Cline, Campaigne, and Spies (49) to investigate the conversion of thioacetophenone to α,α'-dimethylstilbene (VI). Copper powder did not react, either when fused with the dry



VI

compound, or when refluxed in boiling xylene, but an 18 per cent yield of VI was obtained when excess Raney nickel was refluxed with trithioacetophenone in boiling xylene. Since no thione was recovered from the reaction, the main product was probably ethylbenzene. The reduction of thiones to hydrocarbons by Raney nickel alone has not been demonstrated, but Bougault, Cattelain, and Chabier (40) found that phenylthiopyruvic acid was converted to β-phenylpropionic acid by Raney nickel in cold aqueous or alcoholic solution.

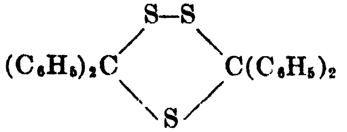
The reaction of alkali metals on thiocarbonyl compounds has not been adequately described. Schönberg (172) noted that alkali metals reacted with xanthione to give colored products which were unstable in air, and may have been the metal ketyls. Bergmann (28) pointed out that thiones react with sodium differently from ketones. No experimental details were given in either of these papers. In those cases where enolization may occur, such as in thioacetoacetic esters (140), alkali metals react to evolve hydrogen and form the metal mercaptides.

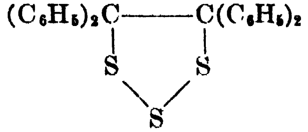
C. OXIDATION

Thiones and thials have been treated with a variety of oxidizing agents. In general, the trimeric thiones and thials behave like sulfides, being converted to the sulfoxides and sulfones. The monomeric thiones usually yield the ketone and sulfur dioxide on oxidation, with intermediate peroxides sometimes formed. The monomeric thiocarbonyl compounds are much less stable toward oxidizing agents than the trimers.

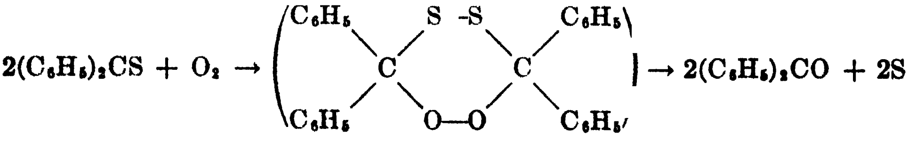
1. Oxidation by air or gaseous oxygen

Thiobenzophenone is unstable in air and must be isolated and stored in an inert atmosphere. Schönberg, Schutz, and Nickel (191) investigated the products formed when thiobenzophenone was exposed to dry air for four weeks, and isolated benzophenone and an unidentified compound, $C_{26}H_{20}S_3$, which is most probably represented by VII or VIII.


VII


VIII

The effect of oxygen on thiobenzophenone has been studied by several workers. Staudinger and Freudenberger (208) found that, contrary to expectation, very little sulfur dioxide was formed when thiobenzophenone was exposed to dry oxygen, but instead benzophenone and a tetraphenyldimethylene trisulfide were formed. This trisulfide is apparently the same as that formed by the action of air on thiobenzophenone. These authors therefore assumed that the first step was unusual, in that oxidation took place on the carbon atom to give the unstable peroxide (IX), which decomposed to benzophenone and nascent sulfur. The nascent sulfur could then combine with two molecules of thiobenzophenone to form the trisulfide.


IX

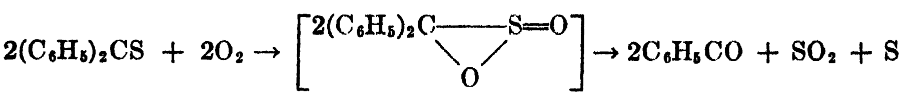
$$2(C_6H_5)_2CS + S \rightarrow C_{26}H_{20}S_3$$

Quantitative estimates of the amount of oxygen used up corresponded very closely to the over-all equation:

$$6(C_6H_5)_2CS + O_2 \rightarrow 2(C_6H_5)_2CO + 2C_{26}H_{20}S_3$$

The similarity between triphenylmethyl and thiobenzophenone in taking up two atoms of oxygen to form an unstable peroxide has been noted by Bergmann *et al.* (31).

Schönberg and Mostafa (180) found that passing oxygen through a benzene solution of thiobenzophenone for 5 hr. produced benzophenone, sulfur, and sulfur dioxide. The reaction was light-catalyzed, since *p,p'*-dimethoxythiobenzophenone, *p,p'*-tetramethyldiaminothiobenzophenone, xanthione, and thioxanthione were almost completely stable to oxygen in the dark, but were readily oxidized to the ketones, sulfur, and sulfur dioxide in bright sunlight. *N*-Phenylthioacridone, 4-thioflavone, and 2,6-diphenyldithiopyrone were almost completely stable even in sunlight. The reaction with oxygen in benzene solution apparently proceeds in the normal manner, oxidation first occurring on the sulfur atom.



$$2(C_6H_5)_2CS + 2O_2 \rightarrow \left[2(C_6H_5)_2\underset{\diagdown O \diagup}{C\text{———}S}{=}O\right] \rightarrow 2C_6H_5CO + SO_2 + S$$

2. Oxidation by hydrogen peroxide

The effect of hydrogen peroxide on the trimethylene trisulfide ring has been described by Hinsberg (87, 88, 89), Fromm and Schultis (70), and Bell and Bennett (27). These authors were interested in preparing the stereoisomeric trimethylene trisulfoxides to prove the structure of the original trisulfides. Bell and Bennett (27) give the most exact conditions for the oxidation of trimethylene trisulfide. Treatment with 27 per cent hydrogen peroxide in acetone at 40°C. for 6 hr. yields the monosulfoxide. The monosulfoxide was converted to a mixture of the disulfoxides by 27 per cent hydrogen peroxide in glacial acetic acid at room temperature for 6 hr. Prolonged oxidation in the glacial acetic acid solution caused the formation of the trisulfoxides.

Kitamura (104) found that diaryl thiones were converted to ketones and sulfur dioxide by hydrogen peroxide in potassium hydroxide solution.

3. Oxidation by potassium permanganate

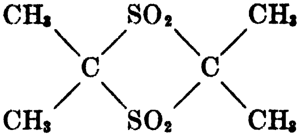
Guareschi (82) and Autenrieth (6) investigated the action of neutral permanganate solutions on trimethylene trisulfides. Guareschi treated trithioacetaldehyde with boiling neutral potassium permanganate solution, and obtained a mixture of the potassium salt of ethane-1,1-disulfonic acid, and a trioxide of the trisulfide compound. Zinc permanganate gave a tetroxide and a pentoxide on similar treatment.

$$(C_2H_4S)_3 \xrightarrow[\text{boiling } H_2O]{KMnO_4} C_2H_4(SO_3K)_2 + C_6H_{12}S_3O_6$$

Autenrieth (6) treated dithioacetone with boiling 5 per cent neutral potassium permanganate, and obtained a compound, $C_6H_{12}S_2O_4$, which he believed to be

$$(C_2H_4S)_3 \xrightarrow[\text{boiling } H_2O]{Zn(MnO_4)_2} C_6H_{12}S_3O_4 + C_6H_{12}S_3O_5$$

tetramethyldimethylene disulfone (X).



X

Baumann and coworkers (12, 13, 14, 15, 16) studied the products of the oxidation of trimethylene trisulfides with acidic permanganate solutions, and found that treatment with potassium permanganate in dilute sulfuric acid at steam bath temperature produced a mixture of trisulfones and disulfone-sulfides. When trithioacetone was thus oxidized (16) a pentoxide, $C_9H_{18}S_3O_5$, was apparently obtained, but it was shown to be a eutectic mixture, since it could be separated into a hexoxide, $C_9H_{18}S_3O_6$, and a tetroxide, $C_9H_{18}S_3O_4$. Camps (45) was able to separate effectively the trisulfone from the disulfone-sulfide of trithioformaldehyde, and noted that the reaction was more efficient at 0°C. than at higher temperatures. Thus, when 5 per cent potassium permanganate in 5 per cent sulfuric acid in an ice bath was used, a 51 per cent yield of the trisulfone and a 33 per cent yield of the disulfone-sulfide was obtained, while at 60–80°C., with the same concentration of reactants, only 35 per cent of the trisulfone and 10 per cent of the disulfone-sulfide were found. Lomnitz (122) prepared the di- and tri-sulfones of trithioacetaldehyde by similar reactions. Chattaway and Kellett (46) were able to prepare the monosulfone-disulfide of trithioacetaldehyde by first preparing the monosulfoxide with hydrogen peroxide, and then oxidizing it to the monosulfone with potassium permanganate in glacial acetic acid.

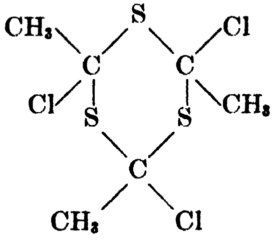
Fromm (66) oxidized several cyclic thiones with potassium permanganate in dilute sulfuric acid. Trithiocyclopentanone gave a trisulfone, but trithiocyclohexanone and trithio-*p*-methylcyclohexanone gave mixtures from which only the disulfone-sulfides were isolated with difficulty. It may be concluded that some steric hindrance is involved in the oxidation of *s*-trithianes to the trisulfones, since while the trisulfones of trithioformaldehyde, trithioacetaldehyde, and trithiocyclopentanone were readily obtained, the trisulfones of trithioacetone, trithiobenzaldehyde, and trithiocyclohexanone were obtained only with difficulty, or not at all.

4. Oxidation by nitric acid

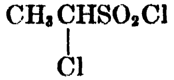
Nitric acid generally reacts too violently with thiones and thials to be of much interest. Husemann (98) claimed to have obtained an oxide of thioformaldehyde on treatment with nitric acid. Fleischer (64) treated a polymer of thiobenzaldehyde with nitric acid, and obtained sulfuric acid and benzoic acid, along with some benzaldehyde and an unidentified compound, C_7H_6SO. Baumann and Fromm (16) obtained an explosive reaction when trithioacetone was treated with concentrated nitric acid but isolated sulfuric acid as one of the products.

5. Oxidation by halogens

Direct chlorination of trithioacetaldehyde in glacial acetic acid replaces the methylene hydrogens, yielding 2,4,6-trimethyl-2,4,6-trichlorotrimethylene 1,3,5-trisulfide (XI) (63). If water is present, however, the chief product is α-chloroethanesulfonyl chloride (XII). Muller and Schiller (146) obtained the α-chlorosulfonyl chloride when a water suspension of trithioacetaldehyde was treated with chlorine. Kostsova (112) obtained chloromethanesulfonyl chloride, or bromomethanesulfonyl bromide, when aqueous suspensions of trithioformaldehyde were treated with chlorine or bromine with cooling. The yield of chloromethanesulfonyl chloride was 51 per cent. Lee and Dougherty (116) carried out the oxidation with chlorine and water in glacial acetic acid, and obtained formaldehyde as one of the products. The equation for the reaction is:



XI



$$CH_3\underset{\substack{|\\ Cl}}{C}HSO_2Cl$$

XII

$$(CH_2S)_3 + 7Cl_2 + 5H_2O \rightarrow 2ClCH_2SO_2Cl + CH_2O + S + 10HCl$$

Baither (8) treated tetramethyldiaminothiobenzophenone with bromine in glacial acetic acid, and obtained an impure unidentified compound which contained 60 per cent of bromine and no sulfur.

D. REDUCTION

The trimethylene trisulfide ring is apparently quite stable toward reducing agents, since compounds of this type have been made by reducing carbon disulfide or phenyl isothiocyanate. Fromm and Ziersch (72) reported that thioacetylthioacetone dimer was quite stable toward zinc and hydrochloric acid. The monomeric thiones behave in general like the analogous ketones toward reducing agents.

1. Clemmensen reduction

Using zinc and hydrochloric acid, Granacher (79) converted phenylthiopyruvic acid to β-phenylpropionic acid. Sen (195), however, obtained the thiol, thioborneol, when thiocamphor was treated with zinc and hydrochloric acid. Schönberg (172) obtained 9,9′-dixanthyl when xanthione was reduced with zinc in glacial acetic acid. The diaryl thiones are probably converted to the methylene derivatives by zinc and acid. Baither (8) obtained *p*,*p*′-tetramethyldiaminodiphenylmethane when Michler's thioketone was treated with zinc dust and steam.

2. Reduction by sodium amalgam

Granacher (79) found that phenylthiopyruvic acid was easily converted to β-phenyl-α-thiolpropionic acid by treatment with sodium amalgam. Spring (204) reported that treatment of dithioacetone with sodium amalgam for two weeks gave isopropyl mercaptan. This reaction has not been confirmed in recent literature, however.

3. Reduction by hydrogen on Raney nickel

Bougault, Cattelain, and Chabrier (40) found that when phenylthiopyruvic acid was treated with Raney nickel in cold aqueous or alcoholic solution, β-phenylpropionic acid was formed.

4. Reduction by sulfides

Hydrogen sulfide or ammonium sulfide will reduce monomeric thiones. Reddelien and Danilof (162) obtained diphenylmethane when excess hydrogen sulfide was used in preparing thiobenzophenone from benzophenone anil.

$$(C_6H_5)_2CS + H_2S \rightarrow (C_6H_5)_2CH_2 + 2S$$

Bergmann, Magat, and Wagenberg (31) noted that thiobenzophenone behaved differently from benzophenone on reduction, since, as with oxidation, the carbon rather than the sulfur is first attacked. Thus benzophenone is first reduced to the pinacol, but thiobenzophenone, on treatment with ammonium bisulfide, yields the disulfide.

$$2(C_6H_5)_2CS \xrightarrow{NH_4HS} (C_6H_5)_2CHSSCH(C_6H_5)_2$$

5. Enzymatic reduction

Neuberg and Nord (148) demonstrated that the thiocarbonyl group may behave like the carbonyl group toward enzyme systems. In their experiments thialdine was used as a source of thioacetaldehyde, since trithioacetaldehyde was insoluble in water solutions. An alcoholic solution of thialdine was added to a fermenting mixture of sugar and water, and within 5 min. ethyl mercaptan was detected in the evolving gases. Yeast killed by boiling was not effective in reducing thioacetaldehyde to ethyl mercaptan

E. REACTION WITH SALTS OF METALS

One of the earliest reactions noted in the thione–thial series was the formation of complex addition compounds with the salts of heavy metals. In 1863, Husemann (98) reported that his "dimethylene sulfur", from methylene iodide and sodium bisulfide, formed salts with mercuric chloride, platinum chloride, and gold chloride. The formation of these complexes was used as a means of confirming the identification of thiones and thials by numerous investigators (14, 127, 203, 224). Hofmann (95) analyzed the silver nitrate and platinic chloride addition compounds of thioformaldehyde and showed them to have the formulas $C_3H_6S_3 \cdot AgNO_3$ and $C_3H_6S_3 \cdot PtCl_4$, thus showing 3 moles of CH_2S per mole of salt, and indicating the trimeric structure for thioformaldehyde. Klinger (107) used the silver nitrate and platinic chloride addition complexes to show the trimeric structure of thioacetaldehyde.

The mercuric chloride addition complex was used by Arndt and Nathwey (3) to isolate the unstable diethyl thiochelidonate. By preparing the thione in the presence of mercuric chloride, the stable complex was obtained. When an ether suspension of this compound was treated with concentrated potassium iodide solution, mercuric iodide was precipitated, and the free thione was obtained.

The nature of these colored complex addition products has been studied by Simonis and Elias (200) and Schönberg (172, 192). The former authors investigated a large series of addition complexes of 2,3-dimethyl-4-thiochromone, and found that the molar ratio of the monomeric thione to metal salt varied with the nature of the solvent as well as with the nature of the salt. When the reaction was run in fuming hydrochloric acid, 2 moles of thione were precipitated with 1 mole of mercuric chloride, but if ether or absolute alcohol was the solvent, the molar ratio was one to one. When fuming hydrochloric acid was used as the solvent, the ratio of thione to metal salt in the complex was 2:1 for platinic chloride, 1:2 for bismuth iodide, and 3:1 for gold chloride. In addition to those already mentioned, complexes with cuprous chloride, cupric chloride, uranium oxychloride, ferric chloride, cadmium iodide, mercuric iodide, silver nitrate, zinc chloride, stannic chloride, and antimony chloride were prepared.

Schönberg (172) noted that when these molecular compounds were formed, a distinct color shift occurred which was probably associated with a structural change. Later, Schönberg and Stolpp (192) investigated the structure of metal salt complexes of diaryl thiones, and found that these compounds behaved like carbonium ions, in which the metal is associated with the sulfur atom. Thus the diaryl thione complexes with mercuric chloride and silver chlorate may be represented as:

$$[\overset{+}{Ar_2C}SHgCl]Cl^- \quad \text{and} \quad [\overset{+}{Ar_2C}SAg]ClO_4^-$$

This concept does not account for the varying molar ratios of thione to salt found by Simonis and Elias.

F. EFFECTS OF ACIDS AND BASES

Baumann and Fromm (15) noted that treatment of the less stable α-trithioaldehydes with acid solutions caused partial inversion to the β-forms, and treatment of the polymeric thioaldehydes with alcoholic hydrogen chloride solution converted the polymers to a mixture of trimers. This reaction was carefully investigated by Suyver (215), who noted that acid catalysts give equilibrium mixtures of α- and β-trithioaldehydes which are the same, whether the pure α- or the pure β-form is used as starting material. The β-form usually predominates in these mixtures. Thus, treatment of α- or β-trithioacetaldehyde with alcoholic hydrogen chloride gives a mixture containing 89 per cent β-trithioacetaldehyde. Hydrogen iodide was used to effect a similar conversion by Fromm and Soffner (71).

When monomeric thiones are boiled in aqueous acid or base, hydrolysis occurs. Baither (8) boiled *p,p'*-tetramethyldiaminothiobenzophenone in hydrochloric

$$Ar_2CS + H_2O \xrightarrow[\text{or } OH^-]{H^+} Ar_2CO + H_2S$$

acid, and obtained Michler's ketone and hydrogen sulfide. Wallach (220) obtained the same result with dilute sulfuric acid. Both Gattermann and Schulze (75) and Vorlander and Mittag (219) obtained benzophenone and potassium sulfide when thiobenzophenone was boiled in alcoholic potassium hydroxide. Thioacridone was converted to acridone by boiling sulfuric acid (Edinger and Arnold (57)). Granacher (79) found that phenylthiopyruvic acid was hydrolyzed to phenylpyruvic acid by boiling ammonium hydroxide solution. Mitra investigated the acidic and basic hydrolysis of thioacetoacetic esters (136, 139), and found that hydrolysis of the thiocarbonyl group occurred along with normal ketonic decomposition of the acids. Thus, when ethyl thioacetoacetate was boiled with 10 per cent sulfuric acid or 10 per cent aqueous potassium hydroxide, the products were acetone, hydrogen sulfide, and carbon dioxide. Ethyl ethylthioacetoacetate yielded hydrogen sulfide, carbon dioxide, and methyl propyl ketone.

Edinger (55, 56) pointed out that thioacridone was soluble in aqueous alkali and behaved in alkaline solution like the tautomeric 9-mercaptoacridine.

The aromatic trithials are quite stable in alkaline solutions. When the monomeric aromatic thials are treated with alkali, however, the Cannizzaro reaction can occur. This condition is obtained when aromatic thials are prepared in alkaline solution. The reaction was first observed by Klinger (108), who attempted to prepare thiobenzaldehyde by treating benzal chloride with excess potassium bisulfide. The products obtained were benzyl disulfide (XIII) and potassium dithiobenzoate (XIV). These same products were obtained when a

$$\underset{\text{XIII}}{C_6H_5CH_2SSCH_2C_6H_5} \qquad \underset{\text{XIV}}{C_6H_5CS_2K}$$

polymeric thiobenzaldehyde (m.p. 80–90°C.) was treated with alcoholic potassium bisulfide, but β-trithiobenzaldehyde did not react. Wood and Bost (226) investigated the conditions of the Cannizzaro reaction with thiobenzaldehyde rather carefully, and found that when thiobenzaldehyde was prepared in alkaline solutions the monomer was first formed, but reacted immediately in several ways. Some trimerized to β-trithiobenzaldehyde, but dismutation occurred with the greater part to form benzyl dithiobenzoate, and a small portion was converted to the benzylmercaptal of thiobenzaldehyde. The reactions occurring when benzal chloride is treated with sodium sulfide in alcoholic solution (1), or when benzaldehyde is treated with hydrogen sulfide in alcoholic sodium or potassium hydroxide solution (1a), are as follows:

$$C_6H_5CHCl_2 + Na_2S \rightarrow C_6H_5CHS + NaCl \tag{1}$$

$$C_6H_5CHO + H_2S \xrightarrow{\text{alcoholic NaOH}} C_6H_5CHS + H_2O \tag{1a}$$

$$3C_6H_5CHS \rightarrow (C_6H_5CHS)_3 \tag{2}$$

$$2C_6H_5CHS \rightarrow C_6H_5CS_2CH_2C_6H_5 \tag{3}$$

$$C_6H_5CS_2CH_2C_6H_5 \xrightarrow{Na_2S} C_6H_5CS_2Na + NaSCH_2C_6H_5 \tag{4}$$

$$C_6H_5CHS + 2NaSCH_2C_6H_5 \rightarrow C_6H_5CH(SCH_2C_6H_5)_2 + Na_2S \tag{5}$$

That thiobenzaldehyde actually dismutates to benzyl dithiobenzoate was demonstrated by distilling β-trithiobenzaldehyde under reduced pressure in the presence of one drop of concentrated sulfuric acid (226). Under these conditions the trimer dissociated to the monomer, part of which reassociated to the trimer, and part of which dismutated to the dithio ester. Treatment of the ester with sodium sulfide caused the hydrolysis to the dithio acid salt and sodium mercaptide.

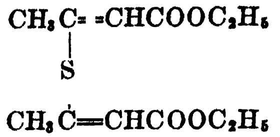
G. KETO-ENOL ISOMERISM

In those cases in which there is a hydrogen atom alpha to a thiocarbonyl group, one would expect keto and enol forms to exist. These forms could not exist if the thione or thial is in the trimeric form, and are therefore unknown among the simple alkyl thiones and thials.

1. *The α- and β-thioketo acids*

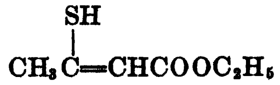
The α-thioketo acids undoubtedly exist in both forms. Although they react readily with ketone reagents, such as phenylhydrazine and hydroxylamine (79, 100, 157), they also react in alkaline solution as thiols. Zipser (230) found that α-sulfhydrylcinnamylacrylic acid readily yielded α-thiobenzylcinnamylacrylic acid when treated with benzyl chloride in alkaline solution.

The thione–thiol isomers have been rather extensively investigated in the β-thioketo acids, particularly in the case of ethyl thioacetoacetate. Scheibler and Bube (167) prepared this compound by treatment of ethyl β-chlorocrotonate with potassium sulfide in alcohol, and obtained a mixture of ethyl di-β-crotonyl sulfide (XV) and ethyl β-mercaptocrotonate (XVI). Later Scheibler, Topouzada, and Schulze (168) found that XVI existed in *cis* and *trans* forms which could be separated with difficulty by repeated fractionation. These authors noted that treatment of the sodium salt of XVI with methyl iodide, benzyl



$CH_3C(=CHCOOC_2H_5)-S-C(CH_3)=CHCOOC_2H_5$

XV

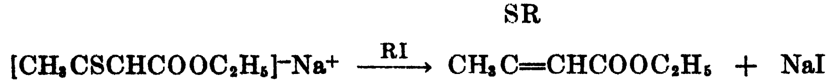


$CH_3C(SH)=CHCOOC_2H_5$

XVI

chloride, or ethyl chloroacetate gave only the thioethers and no alkylation of the α-carbon, and therefore concluded that the compound did not exist in the keto form. Mitra undertook the investigation of thioacetoacetic esters, and reported the results in a series of papers (136–143). It was found that these compounds gave reactions of both thione and thiol types. Thus, they reacted with hydroxylamine to evolve hydrogen sulfide, gave pyrazolones with phenylhydrazine, and were hydrolyzed by acidic or basic solutions to give ketones. However, the sodium derivatives always gave the thioethers with alkyl halides,

$$\mathrm{XVI} \xrightarrow[H^+ \text{ or } OH^-]{H_2O} CH_3COCH_3 + CO_2 + C_2H_5OH + H_2S$$



$$[CH_3CSCHCOOC_2H_5]^-Na^+ \xrightarrow{RI} CH_3C(SR)=CHCOOC_2H_5 + NaI$$

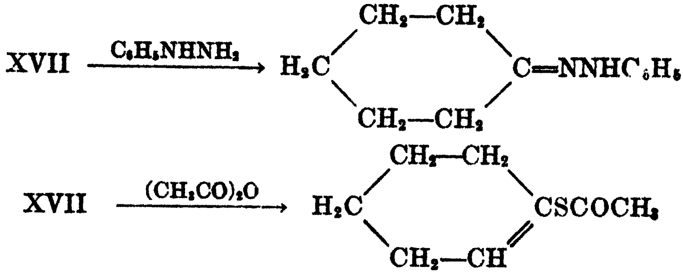
indicating complete conversion to the thiol phase. The per cent of thiol in the equilibrium at various temperatures was estimated by Mitra (143) for thioacetoacetic ester and several α-substituted thioacetoacetic esters. The procedure was to maintain the compound in alcohol in a thermostat at the required temperature for 6 hr., then quickly transfer it to an iodine solution in alcohol at −7°C., and titrate the excess iodine with sodium thiosulfate. The iodine oxidizes the thiol to the disulfide without affecting the thione. Mitra's results are summarized in table 1, from which it is evident that there is a shift toward the thione phase as the temperature is increased, and that substitution on the α-carbon increases the thiol phase.

TABLE 1

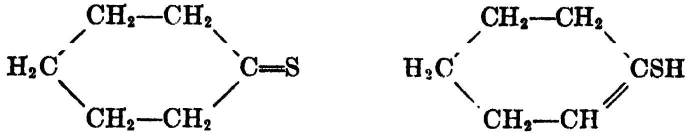
$CH_3CSCHRCOOC_2H_5$	PER CENT THIOL IN EQUILIBRIUM AT GIVEN TEMPERATURE		
	30°C.	40°C.	60°C.
1. R = H	41.0		38.7
2. R = CH_3	62.8	61.9	60.0
3. R = $CH_2CH(CH_3)_2$			64.4
4. R = $CO_2C_2H_5$	61.1		58.5

2. The cyclic thiones

Sen (196) found that monomeric cyclohexanone gave both ketone derivatives, such as the carbazone and phenylhydrazone, and mercaptan derivatives, such as the thiomethyl derivative with methyl sulfate, and the acetyl derivative with



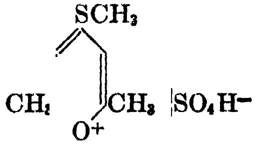
acetic anhydride. These reactions indicated the existence of the thione–thiol equilibrium:



XVII

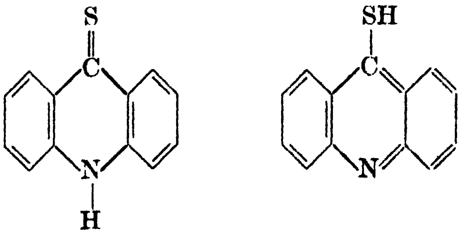
Using the iodine oxidation method, Sen found that there was 38 per cent thiol in freshly distilled thiocyclohexanone, and 70 per cent thiol in a preparation 1 hr. old, a result which would indicate that the thiol tautomer is more stable.

Reactions in the heterocyclic thione series indicate that these compounds probably exist in both thione and thiol forms. Hantzch (85) noted that treatment of 2,6-dimethylthiopyrone with methyl sulfate gave a thiomethyl oxonium salt (XVIII).



XVIII

Edinger and Arnold (56, 57) noted that thioacridone gave acridone in boiling sulfuric acid, but yielded 9-thiobenzylacridine with benzyl chloride in alkaline solution. The existence of the thione–thiol isomers in thioacridone (XIX)



XIX

was also confirmed by Gleu and Schaarschmidt (77) and by Chernstov (47). Gleu and Schaarschmidt found that alkylation of thioacridone gave the *S*-

alkyl derivatives exclusively, and these could not be rearranged to the *N*-alkyl derivatives by heat. The equilibrium has not been estimated quantitatively.

H. CARBONYL REAGENTS

The dimeric and trimeric thiones and thials do not react with carbonyl reagents, unless dissociated in some manner. However, the monomeric thiones readily form derivatives with the usual carbonyl reagents, such as hydroxylamine, phenylhydrazine, etc., reacting to split out hydrogen sulfide instead of water. This is good evidence that the α- and β-thioketo acids are monomers, since they react with these reagents (79, 136, 157). As previously noted, thioacetoacetic esters react like acetoacetic esters with phenylhydrazine to give the pyrazolones.

The diaryl thiones react readily with carbonyl reagents. Baither (8, 9) investigated the reactions of *p,p'*-tetramethyldiaminothiobenzophenone and found that it gave the oxime and phenylhydrazone of Michler's ketone. The thione also reacted with aniline to give the anil. Bergreen (33) and Gattermann and Schulze (75) prepared the oxime and phenylhydrazone of thiobenzophenone, and found them to be identical with those prepared from benzophenone itself.

The monomeric cyclic thiones also give carbonyl derivatives. Sen (195) prepared the camphor oxime, phenylhydrazone, and semicarbazone from thiocamphor, and also prepared the semicarbazones and phenylhydrazones from thiocyclohexanone and thiocyclopentanone (196). Graebe and Roder (78) obtained xanthone oxime and xanthone phenylhydrazone from xanthione. Simonis and Rosenberg (201) found the thiocarbonyl group in various thiochromones to react readily with hydroxylamine and phenylhydrazine.

I. ALKYL HALIDES

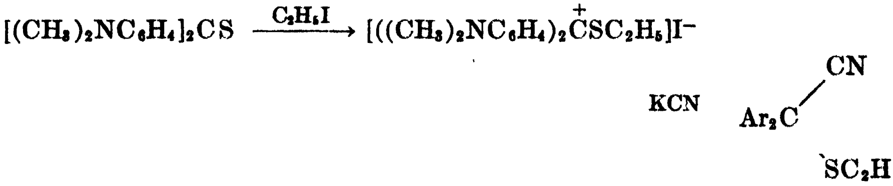
Alkyl halides react with thials and thiones in several ways. Early investigators (Marckwald (129); Baumann and Fromm (15)) noted that when α-trithioacetaldehyde or polymeric thioacetaldehyde was treated with methyl or ethyl iodide, it was converted to the more stable β-isomer. Mann and Pope (125) reported that their γ-trithioacetaldehyde was converted to the β-compound by methyl iodide. Alkyl halides have also been found to react with trithials and trithiones to produce halogenated sulfur compounds. Klinger (106) gives the following equation:

$$(CH_3CHS)_3 + 3CH_3I \rightarrow (CH_3)_3SI + CH_3CH(SCHICH_3)_2$$

Platonov and Anisimov (156) found that trialkylsulfur iodides were obtained in every case where a trithial was treated with an alkyl iodide at 100–110°C. for 20 hr. Alkyl bromides were not very reactive.

The alkylation of ethyl thioacetoacetate has been investigated by Ray, Mitra, and Ghosh (161). The thioethers were obtained in every case when the sodium derivative of ethyl thioacetoacetate was treated with an alkyl halide, such as ethyl iodide, propyl iodide, amyl bromide, benzyl chloride, or phenacyl bromide. This is therefore a reaction of the mercaptan group, rather than a thione reaction.

Several reactions of diaryl thiones with alkyl halides have been reported. Baither (9) found that when *p,p'*-tetramethyldiaminothiobenzophenone was treated with benzyl chloride in carbon disulfide solution, dibenzyl sulfide and *p,p'*-tetramethyldiaminobenzophenone dichloride were formed. Madelung (123) obtained a highly colored cyanide by treating *p,p'*-tetramethyldiaminothiobenzophenone with ethyl iodide and potassium cyanide. Since the cyanide could be prepared in another way, the structure of the carbonium ion formed by

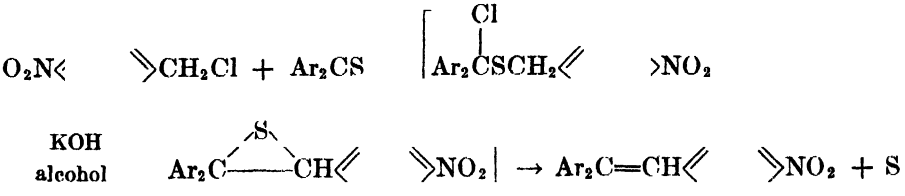


$$[(CH_3)_2NC_6H_4]_2CS \xrightarrow{C_2H_5I} [((CH_3)_2NC_6H_4)_2\overset{+}{C}SC_2H_5]I^- \xrightarrow{KCN} Ar_2C(CN)(SC_2H_5)$$

addition of the alkyl halide is probably correct. Alkyl halides probably react with diaryl thiones in two steps:

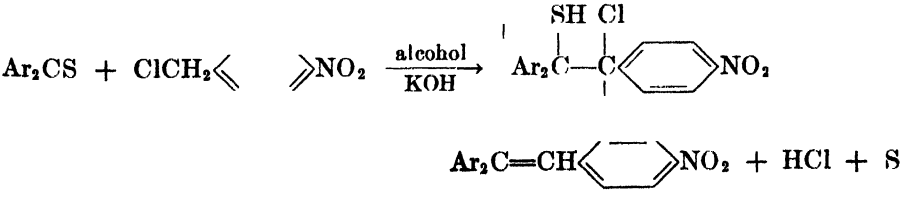
$$Ar_2CS \xrightarrow{RX} [Ar_2\overset{+}{C}SR]X^- \xrightarrow{RX} Ar_2CX_2 + R_2S$$

A similar mechanism is postulated for the reaction of *p*-nitrobenzyl chloride with diaryl thiones by Bergmann and Hervey (30). When Michler's thioketone was treated with *p*-nitrobenzyl chloride in alcoholic potassium hydroxide, the triarylethylene (XX) and sulfur were obtained. The reaction may be pictured as follows:

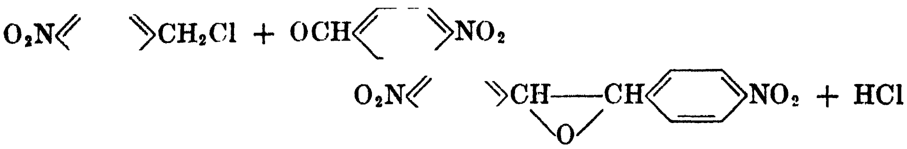


XX

Hahn (84) believed that the reaction was of an aldol type and represented it thus:

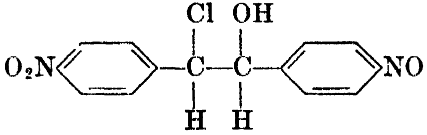


The evidence for this mechanism was based on the reaction of *p*-nitrobenzyl chloride with *p*-nitrobenzaldehyde to give an ethylene oxide derivative (XXI).



XXI

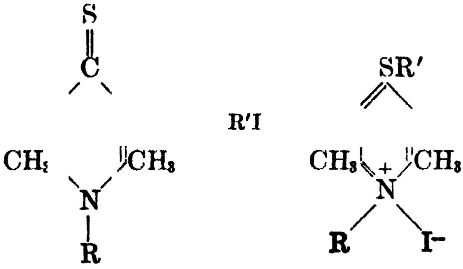
Hahn therefore assumed that the chlorohydrin XXII was an intermediate.



XXII

The analogy with thiocarbonyls is not conclusive however, since these compounds do not necessarily behave like carbonyls.

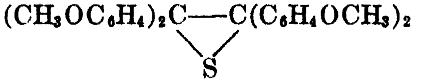
The effect of alkyl iodides on *N*-alkylthiopyridones was investigated by Michaelis and Holken (134), who observed that the thiones were readily converted to the thioalkylpyridinium iodides (XXIII) at ordinary temperatures.



XXIII

J. GRIGNARD REAGENTS

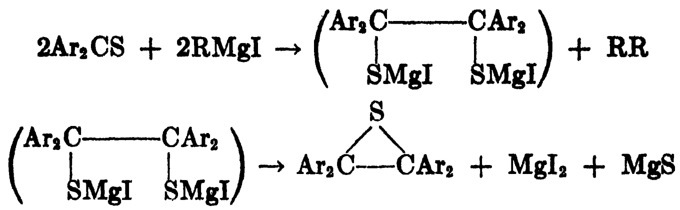
The Grignard reagent reacts differently with thiones than with ketones. The reaction has been investigated by Schönberg and coworkers, who found that when di-*p*-anisyl thione was treated with phenylmagnesium bromide or α-naphthylmagnesium bromide, the ethylene sulfide XXIV was formed (172). Schönberg, Schutz, and Marschner (189) treated thiobenzophenone with magnesium subiodide and obtained tetraphenylethylene sulfide. Since the same



$$\underbrace{(CH_3OC_6H_4)_2C{-\!-}C(C_6H_4OCH_3)_2}_{S}$$

XXIV

product is obtained with Grignard reagents, the mechanism of the Grignard reaction was postulated as follows:



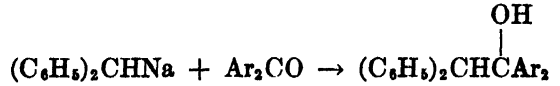
$$2Ar_2CS + 2RMgI \rightarrow \left(\begin{matrix} Ar_2C & \text{---} & CAr_2 \\ | & & | \\ SMgI & & SMgI \end{matrix}\right) + RR$$

$$\left(\begin{matrix} Ar_2C & \text{---} & CAr_2 \\ | & & | \\ SMgI & & SMgI \end{matrix}\right) \rightarrow Ar_2C\overset{S}{\text{---}}CAr_2 + MgI_2 + MgS$$

A variety of alkyl and aryl Grignard reagents were used by Schönberg, Rosenbach, and Schutz (182), and the ethylene sulfide was obtained in every case. Phenylmagnesium bromide gave the highest yield (about 70 per cent) of the ethylene sulfide, while ethylmagnesium bromide gave low yields. In some cases, such as xanthione, the ethylene sulfide was unstable, decomposing spontaneously to the ethylene derivative and sulfur.

K. METAL ALKYLS

Bergmann and Wagenberg (32) investigated the reaction of diphenylmethylsodium on aromatic ketones and thiones, and found that the reactions follow the same course, but that the mercaptans lose hydrogen sulfide more readily than the alcohols lose water, so that the ethylene derivative is usually isolated as the product of the thione reaction. The thiones used were thiobenzophenone, di-*p*-anisyl thione, and *p*,*p*′-tetramethyldiaminothiobenzophenone.

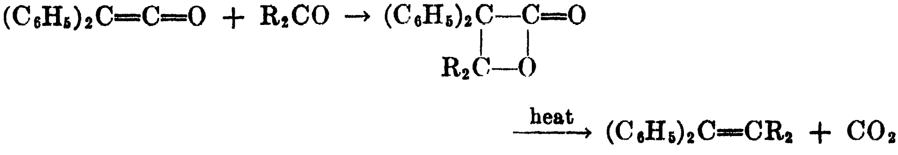


$$(C_6H_5)_2CHNa + Ar_2CO \rightarrow (C_6H_5)_2CH\overset{\overset{OH}{|}}{C}Ar_2$$

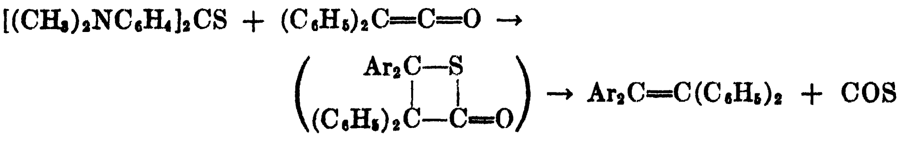
$$(C_6H_5)_2CHNa + Ar_2CS \rightarrow (C_6H_5)_2C{=}CAr_2 + H_2S$$

L. DIPHENYLKETENE

Diphenylketene reacts with ketones to give a lactone which decomposes on heating to carbon dioxide and the ethylene derivative (Staudinger and Kon (210)). Staudinger (205) found that diaryl thiones behave in two ways toward diphenylketene. The negatively substituted *p*,*p*′-tetramethyldiaminothiobenzophenone reacted like ordinary ketones, to give an unstable intermediate which decomposed to the ethylene derivative and carbon oxysulfide. With

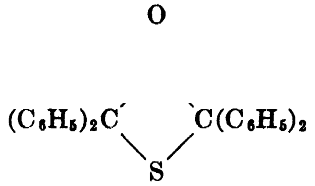


$$(C_6H_5)_2C{=}C{=}O + R_2CO \rightarrow \begin{matrix} (C_6H_5)_2C & \text{---} & C{=}O \\ | & & | \\ R_2C & \text{---} & O \end{matrix} \xrightarrow{\text{heat}} (C_6H_5)_2C{=}CR_2 + CO_2$$



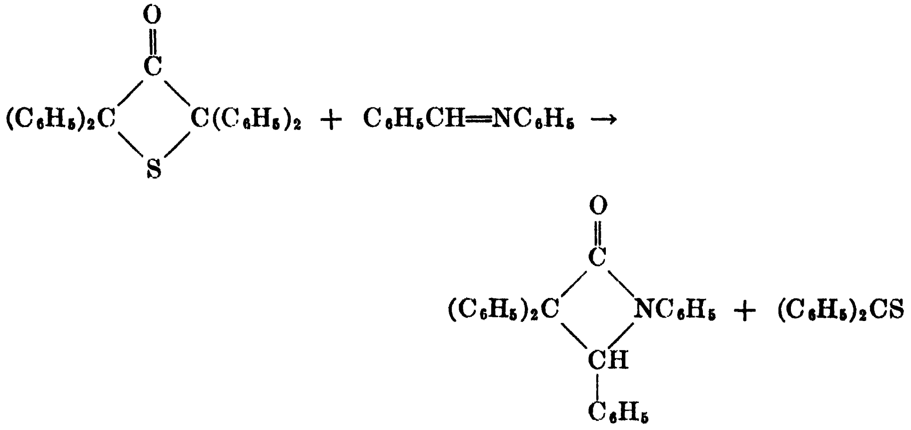
$$[(CH_3)_2NC_6H_4]_2CS + (C_6H_5)_2C{=}C{=}O \rightarrow \left(\begin{matrix} Ar_2C & \text{---} & S \\ | & & | \\ (C_6H_5)_2C & \text{---} & C{=}O \end{matrix}\right) \rightarrow Ar_2C{=}C(C_6H_5)_2 + COS$$

thiobenzophenone or di-*p*-anisyl thione, however, a different product was obtained. When thiobenzophenone was treated with diphenylketene, a stable crystalline sulfur compound, $C_{27}H_{20}OS$, melting at 180–181°C., was obtained. On melting, it dissociated to thiobenzophenone and diphenylketene, but recombined on cooling. This compound was assigned structure XXV by Staudinger. A similar reaction was obtained with di-*p*-anisyl thione. This compound



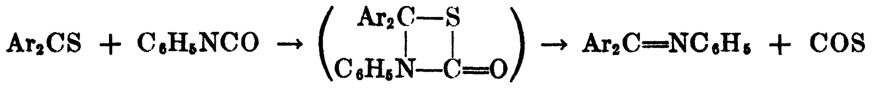
XXV

(XXV) was later used by Staudinger and Freudenberger (207) to purify thiobenzophenone. Impure thiobenzophenone was reacted with diphenylketene, and compound XXV was isolated and heated with benzaldehyde anil at reduced pressure until pure thiobenzophenone distilled.



M. PHENYL ISOCYANATE

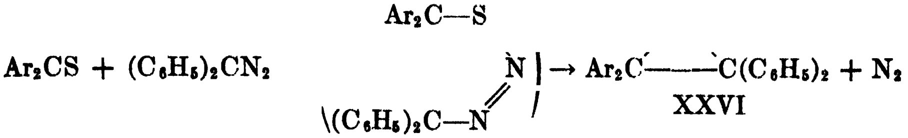
Staudinger and Endle (206) point out that phenyl isocyanate reacts like ketene at elevated temperatures. With *p*,*p*′-tetramethyldiaminothiobenzophenone, the products are the ketone anil and carbon oxysulfide, which may be derived through the cyclic four-membered ring.

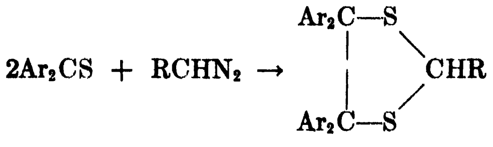


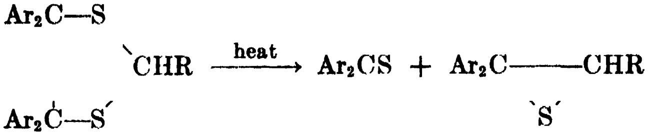
$$Ar_2CS + C_6H_5NCO \rightarrow \left(\begin{array}{l} Ar_2C{-}S \\ C_6H_5N{-}C{=}O \end{array}\right) \rightarrow Ar_2C{=}NC_6H_5 + COS$$

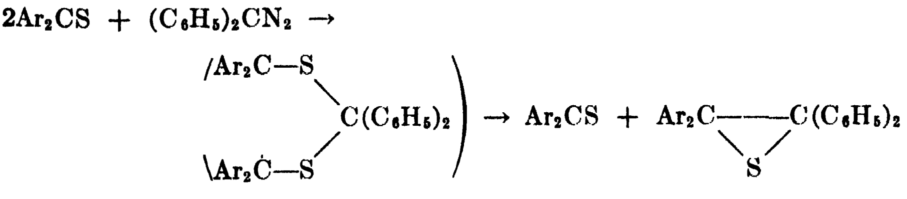
N. ALIPHATIC DIAZO COMPOUNDS

Diazomethane reacts differently with thiones than with ketones because the thiocarbonyl group is more highly polarized, according to Meerwein, Bersin, and Burneleit (130). Staudinger and Siegwart (212) caused several diaryl thiones to react with diphenyldiazomethane, and obtained the corresponding tetraarylethylene sulfide (XXVI) and nitrogen. These authors assumed that an unstable nitrogen compound was first formed. Bergmann, Magat, and Wagenberg (31) reacted diazomethane with diaryl thiones, and obtained a stable compound containing a trimethylene disulfide ring (XXVII). This work was repeated by Schönberg, Cernik, and Urban (177), who used diazoethane and ethyl diazoacetate, as well as diazomethane in these reactions. In each case, the trimethylene disulfide compound (XXVII), in which R equals —H, —CH_3, or —$COOC_2H_5$, was obtained. These authors found that when compound XXVII was subjected to heat, it decomposed to give the thione and ethylene sulfide, and also noted that when R was CH_3 or $COOC_2H_5$, decomposition occurred more readily. It was therefore assumed that the reaction with diphenyldiazomethane actually followed the same course as other substituted diazomethanes, but that the intermediate hexaaryltrimethylene disulfide (XXVIII) was unstable. Schönberg and Nickel (181) found that xanthione, thiochromone, and several of the thioflavones reacted with aliphatic diazo compounds in the same way, yielding ethylene sulfides with diphenyldiazomethane, and trimethylene disulfides with diazomethane.


XXVI

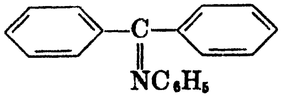

XXVII



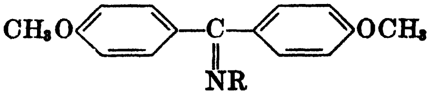

XXVIII

O. PHENYL AZIDE

Schönberg and Urban (193) found that although azides do not react with ketones, they react quite readily with thiones to form Schiff's bases. The following Schiff's bases were obtained by reacting the azide with the thione:

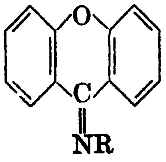


XXIX



XXX

a: R = C_6H_5
b: R = α-$C_{10}H_7$
c: R $CH_2C_6H_5$

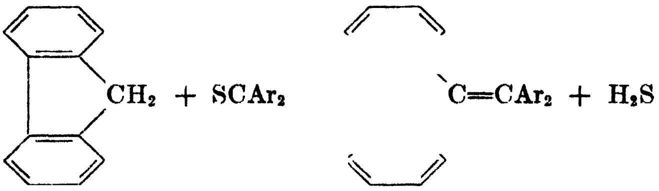


XXXI

a: R = C_6H_5
b: R = $SO_2C_6H_5$

P. DIARYLMETHANES

Schönberg (172) reported that when fluorene was fused with diaryl thiones, hydrogen sulfide was evolved, and the biphenylenediarylethylenes were formed.

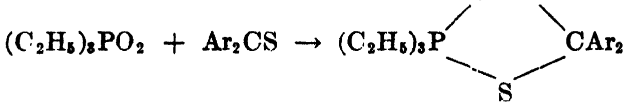


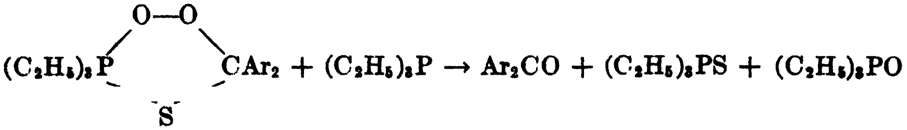
A similar reaction was observed between xanthene and xanthione (188).

Q TRIETHYLPHOSPHINE

Triethylphosphine does not react with thiones in the absence of air, even at the boiling point. Schönberg and Krukll (179) found that in boiling toluene,

$$(C_2H_5)_3P + O_2 \rightarrow (C_2H_5)_3PO_2$$





however, in the presence of dry air, the diaryl ketone, triethylphosphine sulfide, and triethylphosphine oxide are formed, and proposed that triethylphosphine peroxide was the active agent. It was found that the alkoxy-substituted diaryl thiones and xanthione reacted with triethylphosphine peroxide, but that *p,p'*-tetramethyldiaminothiobenzophenone did not.

VII. DETECTION OF THIALS AND THIONES

The presence of monomeric thiones may be detected by their intense colors. Feigl and Bondi (61) found that a reaction occurred between silver saccharide and monomeric thiones to precipitate silver sulfide, and suggested the usefulness of this reaction in the identification of thiones. Later Feigl (60) and Feigl and Dacorso (62) found that the reaction of iodine with sodium azide was greatly enhanced by the catalytic effects of divalent sulfur compounds, and

$$2NaN_3 + I_2 \rightarrow 2NaI + 3N_2$$

suggested the use of this reaction to detect very small quantities of thiones.

VIII. USES OF THIALS AND THIONES

No significant uses have yet been reported for thials and thiones. However, several patents suggest uses to which these compounds might be put. Möller (145) discussed the use of trithioformaldehyde in tanning, since it had been found that this material could replace sulfur in the tanning process. Delson (52) reports that thioacrolein is germicidal and non-poisonous, and therefore suitable for skin ointments and internal administration. Kodak, Ltd. (109) has patented a process for the production of thiones, and their use as sensitizers for photographic emulsions.

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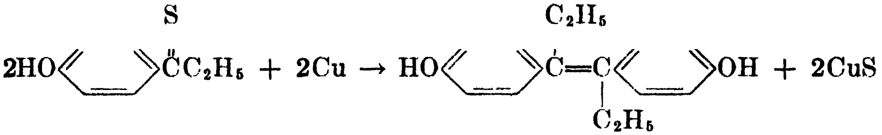
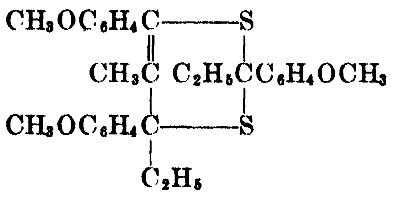
X. ADDENDUM

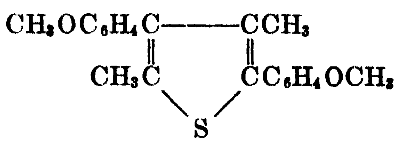
Since this review was submitted for publication, the following information has been obtained. Linnell and Sharma (235) proposed to synthesize α,α'-diethylstilbestrol by condensing *p*-hydroxythiopropiophenone or *p*-methoxythiopropiophenone with copper powder, according to the reaction:



However, attempts to synthesize the required thiones were unsuccessful. *p*-Hydroxypropiophenone yielded an unidentified, red, sulfur-containing compound when treated with hydrogen sulfide and hydrogen chloride in alcohol solution. *p*-Methoxypropiophenone when treated with these reagents yielded a white crystalline compound (I) which, on being heated with copper bronze, yielded a stable sulfur-containing compound (II). Linnell and Sharma believed that compound I was 2,4,5-tri-*p*-anisyl-2,4,5-triethyltrimethylene-1,3-disulfide, and that compound II was 2,3,5,6-tetra-*p*-anisyl-2,3,5,6-tetraethyl-1,4-dithiane. However, a comparison of the physical properties and analyses indicates that these two compounds are identical with the compounds prepared from *p*-methoxypropiophenone by Campaigne (232), which were shown to be "anhydrotri-*p*-methoxypropiophenone disulfide" (III) and 2,4-di-*p*-anisyl-3,5-dimethylthiophene (IV), respectively.



III



IV

Linnell and Shaikmahamud (234) treated 2-ethyl-4-methoxybenzaldehyde with hydrogen sulfide in cold alcohol containing a trace of piperidine, and obtained what was undoubtedly a polymeric thial, although the molecular weight was not determined. This compound was converted to 2,2′-diethyl-4,4′-dimethoxystilbene, an isomer of α,α'-diethylstilbestrol, by heating with copper powder.

Bergmann and Israelashwili (231) studied the conversion of the trimeric 9-phenanthrenethial to the corresponding ethylene derivative by heating with copper or nickel. Copper was found to give a mixture of the ethylene derivative and the disulfide, but nickel yielded the pure ethylene derivative in 20 per cent yield.

Another use of thiones is suggested by a recent British patent (233) for therapeutic ointments which contain either monomeric or polymeric thiocyclohexanone, ethyl methyl thione, or diethyl thione.

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THE FRACTIONATION OF HIGH-POLYMERIC SUBSTANCES[1]

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I. INTRODUCTION

A. GENERAL

A polymer is a compound[3] each molecule of which is formed (except for end groups) of a given number of structural units closely related to the molecules of the monomer (or monomers) from which the polymer is derived. It has, therefore, like other covalent compounds, a molecular weight; if its molecular weight is very large, it is a "high" polymer. Many high-polymeric substances are known, and as a class they are of great and increasing importance; yet high polymers in pure form are not known. Both the natural and synthetic high-polymeric substances are mixtures (2, 11, 18, 70, 177, 268); individual molecules may differ in size (i.e., in the number of repeating units, or, as it is often called, the degree of polymerization), in shape (i.e., in the degree of branching or cross-linking), and even in chemical composition (as, for example, in the case of nitrated cellulose). The important names in high-polymer chemistry, such as "cellulose", do not refer as in classical chemistry to pure chemical compounds; rather they are generic, denoting mixtures of compounds whose molecules, though very similar, may differ in size, shape, and composition. It is understandable therefore why the term "high polymer" has come to have a similarly generic meaning and why in general usage it signifies a high-polymeric substance rather than a high-polymeric compound. As this usage, although a bit confusing, is both common and convenient, it will be adopted frequently in this review.

High-polymeric systems may, however, be homogeneous in all respects but molecular size. Staudinger (17) has introduced the term "homologous polymeric series" for a series of linear (unbranched) polymers whose members differ in degree of polymerization but not in chemical composition. Many high-polymeric substances are found to be mixtures of members of such homologous polymeric series.

The fact that high polymers are heterogeneous is of tremendous importance; to their very heterogeneity they owe many of the properties that make them so interesting and useful. But it is important to realize that, being non-uniform, they are infinitely variable. The molecular-weight distribution of a high polymer, for example, may vary from sample to sample; with natural products it depends on the source of the material, with synthetics on the method of preparation, and with both on previous treatment such as purification, bleaching (of cellulose), or milling (of rubber). Therefore, in the interpretation and use of a measured value of any property that is a function of molecular weight, such as osmotic pressure or solution viscosity, it must be clearly recognized (*1*) that two samples giving the same value may yet be very different in other respects because of a different molecular-size distribution and (*2*) that a "molecular weight" calculated from such a value will be merely an average value. Indeed, as Kraemer (150) (as well as others) has pointed out, the average molecular weight deduced from osmotic-pressure data is different from that deduced from viscosity data, because these properties are different functions of the molecular distribution. As many of the industrially important properties of high polymers likewise depend on the shape of the distribution curve, it is highly important that methods be available (*1*) for determining the molecular-weight distribution in the heterogeneous material without necessarily separating it into homogeneous fractions, and (*2*) for preparing fractions at least approaching homogeneity with respect to molecular weight, in order to make it possible to determine the true relation between a given property and molecular weight. Such fractionation methods, fortunately, have been and are being developed; the first type will hereafter be called analytical, the second (with which this review is primarily concerned) will be called preparative.

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[3] NED defines "polymer" as (in part)" . . . any one of a series of polymeric compounds"; Webster's *New International Dictionary* (2nd edition, unabridged) defines it as " . . . any of two or more polymeric compounds."

B. HISTORICAL

The idea that high-polymeric materials might be heterogeneous is not new. As far back as 1887 (79), 1888 (106), and 1900 (295, 296), natural rubber was believed to consist of two compounds, one soluble and one insoluble in organic solvents such as chloroform or carbon disulfide. (Later, ethyl ether (84) and petroleum ether (51, 84) were found more suitable for separating the two fractions.) Thus the earliest fractionation method was an extraction.

Fractional precipitation, which is now the most widely used fractionation method, was at first used for the purpose of purification (of rubber, by Caspari (51) in 1913) and only later for the separation of fractions (from nitrocellulose by Duclaux and Wollman (74) in 1920). It quickly became popular in the cellulose field, and was adapted to balata (271) and to various synthetic polymers (267, 269, 272, 273, 275–277, 280, 281) by Staudinger and his coworkers, beginning in 1927, and to rubber by Midgley and his associates (189) in 1931.

Fractional solution methods, although claimed by some to be superior to precipitation, have never come into such wide use. They were introduced by Craik and Miles (57) in 1931 and have been carefully studied in more recent years by Bloomfield and Farmer (39), Kemp and Peters (141), and others.

Other methods such as those involving ultracentrifugation or chromatographic adsorption have been used, but they are of much less general applicability. The ultracentrifuge has been shown (148, 150, 257, 258) to be well suited to analytical determination of heterogeneity, but cost and complexity have limited its use.

On the whole, there has been a steadily increasing recognition of the importance of fractionation both in research and for industrial control. Fractionation is an essential preliminary step in the application of viscosity measurements to the determination of the average molecular weight of a high-polymeric material; it makes possible the correlation of other physical properties with the average molecular weight and with the molecular-weight distribution; and it is indispensable in research on the kinetics of polymerization and depolymerization.

The growing interest in fractionation is evidenced by the increase in the number of papers published, dealing with fractionation, from three in the period 1920–24 to at least sixty in the period 1935–39.[4]

Reports of research studies involving methods for the fractionation of high-polymeric substances are scattered through many journals of various types, and often appear in papers devoted in large part to other matters. In this survey an effort has been made to collect and systematize such information concerning fractionation methods as has appeared in the literature to the end of 1944.

II. Fractionation Methods

In a discussion of fractionation methods classification is essential, but the classification might be based on any one of several considerations: the purpose of the fractionation,[5] the material fractionated, the principle underlying the method of separation. For the convenience both of those interested in the general subject of fractionation and of those more concerned with its application to a given type of high-polymeric system, the methods have been classified here on the basis of the separation principle, each class being further subdivided according to the material to which the method is applied.

	PRINCIPLE ON WHICH SEPARATION IS BASED
I. Solubility methods	Solubility decreases with molecular weight
1. Fractional precipitation	
(a) By addition of precipitant	
(b) By cooling	
2. Fractional solution	
(a) Solvent of varying composition	
(b) Varying temperature	
3. Distribution between two immiscible solvents	Distribution coefficient depends on molecular weight
II. Rate-of-solution method (diffusion into a single solvent)	Smaller molecules diffuse faster
III. Ultracentrifuge	Sedimentation velocity increases with molecular weight
IV. Chromatographic adsorption	Smaller molecules are preferentially adsorbed
V. Ultrafiltration through graded membranes	Sieving action
VI. Molecular distillation	Larger molecules are less volatile

A. Solubility methods

The solubility methods for fractionating heterogeneous high-polymeric substances depend on the greater solubility in a given liquid of the lower-molecular-weight species, and on the fact that the solvent power of a binary liquid mixture (of solvent and non-solvent) depends on the proportion of the two liquid components. If a non-solvent (also often called the precipitant) is added to a polymer–solvent system, as in fractional precipitation, or a polymer is added to a solvent–non-solvent mixture, as in fractional solution, two phases are obtained at equilibrium, if the proportions of the components are properly adjusted. The upper layer is a solution in which polymer is present in low concentration; the lower layer, or "precipitated" phase, is either a swollen gel or a very viscous liquid, and contains a high proportion of polymer. The material of higher molecular weight tends to concentrate in the precipitated phase, that of lower molecular weight in the supernatant liquid.

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[4] It need hardly be mentioned that the number of papers published during the war years is no index of the recent activity in this field.

[5] The distinction between preparative and analytical methods, for example, has already been mentioned.

One of the earliest theories of solubility fractionation[6] was that of Brønsted (42). He suggested that when we consider only the members of a single homologous polymeric series the potential energy of the polymer molecules is proportional to the molecular weight, and the distribution of the molecules between the two phases is determined by a difference of potential energy, the less mobile large molecules collecting in the phase with the lower potential energy (the precipitated phase), the smaller and more mobile ones in the supernatant liquid. He derived the equation

$$\ln \frac{c'}{c''} = \lambda M/RT$$

where c' and c'' are the concentrations of polymer in the two phases at equilibrium, M is the molecular weight of polymer, and λ is a constant characteristic of the polymer–solvent system but independent of M.

Schulz (244, 246, 253) developed these ideas further by assuming that in the case of binary liquid mixtures λ is a linear function of the liquid composition and showed that the equation

$$\gamma^* = A + B/M \tag{2}$$

adequately expresses the relation between γ^*, the "critical" liquid composition at the precipitation point, and the molecular weight, M, of the polymer; A and B are empirical constants. He also applied the theory to heterogeneous polymers, using a rather arbitrary modification of equation 1, and concluded that the efficiency of fractionation is improved by keeping the concentration of polymer in the supernatant phase as low as possible.

The Brønsted–Schulz theory was remarkably successful in predicting the solubility behavior of high-polymer solutions. However, it was soon suspected that the entropy of mixing of polymer and solvent molecules was a factor of importance and should not be neglected in developing the theory of solubility.

---

[6] In his report on "The Physical Chemistry of Rubber Solutions" Gee (100) has ably and critically reviewed contributions to the theory of the solubility and fractionation of high polymers up to 1943. See also his somewhat later review, "The Thermodynamic Study of Rubber Solutions and Gels," in *Advances in Colloid Science*, Vol. II, H. Mark and G. S. Whitby (*Editors*), pp. 145–95. Interscience Publishers, Inc., New York (1946).

Polymer molecules, in general flexible rather than rigid (8), should be capable of assuming a greater number of random configurations in solution than in the solid state (9), and longer molecules a greater number than shorter ones. Mark (7) assumed that although the decrease in solubility with increasing molecular weight is due principally to the increase in heat of solution, the increase in entropy on solution should make this decrease in solubility less rapid than would be expected if the heat of solution were the only factor. Furthermore, this entropy effect should become more important as the chain length increases. Gee and Treloar (104) measured the free energies and heats of solution and dilution for the system rubber–benzene, and from these values calculated the entropies of solution and dilution. The entropy of solution so determined was, as expected, very much greater than the ideal value. From the results of this investigation, Gee and Treloar concluded that "the main factor governing the solution of rubber is the abnormally large entropy of solution", a factor that had been completely neglected by Brønsted and Schulz.

An explanation for the anomalously large entropy of mixing had already been proposed by Meyer (185). He suggested that the deviation is due not only to the flexibility of the polymer molecules but also to the vast differences in size of the solvent and solute molecules (in the statistical calculation of the number of possible configuration of the system, we cannot imagine one solvent molecule replacing one solute molecule, as we do in solutions of substances with molecular weights of the same order of magnitude). As a model for a solution of a high polymer in a low-molecular liquid he proposed a lattice of $N_1 + nN_2$ sites, to be occupied by N_1 solvent molecules and N_2 polymer molecules, each of the latter consisting of n submolecules of a size comparable to that of molecules of solvent. Using this model, Flory (88, 89) and Huggins (121, 122, 123),[7] independently of each other, calculated the entropy of mixing and the activities of the components of a high-polymer solution. In outline, their argument is somewhat as follows: First, the number of different ways, ϕ, of placing the solvent molecules and polymer submolecules in the lattice are calculated, assuming for the moment complete flexibility at each junction between submolecules (this involves the assumption of unrestricted rotation around carbon–carbon single bonds), and neglecting certain minor complicating factors, such as crossing of the chains. Then, by the use of Boltzmann's equation

$$S = k \ln \phi \tag{3}$$

the entropy of solution of each component can be found. Assuming the heat of solution to be given by a Scatchard–Hildebrand formula

$$\bar{H}_1 - H_1^0 = kV_1\mathbf{V}_2^2 \tag{4}$$

($\bar{H}_1$ is the partial molar heat content of solvent in the solution, H_1^0 the molar heat content of pure solvent, K an empirical constant, V_1 the molar volume of solvent, and $\mathbf{v}_2$ the volume fraction of polymer in the solution), the free energy of solution can be found, and from it the activity; for

---

[7] See also 5, 124, 125, and the more recent summary (Polymer Bull. **1,** 25–30 (1945)).

$$(\bar{H}_1 - H_1^0) - T(\bar{S}_1 - S_1^0) = \bar{F}_1 - F_1^0 = RT \ln a_1 \tag{5}$$

The equation finally derived is, in Huggins' notation,

$$\ln a_1 = \ln V_1 + (1 - \bar{V}_1/\bar{V}_2)\mathbf{v}_2 + \mu \mathbf{v}_2^2 + \text{higher powers of } \mathbf{v}_2 \tag{6}$$

where $\bar{V}_1$ and $\bar{V}_2$ are the partial molar volumes of solvent and polymer, and μ is a constant characteristic of the polymer–solvent system, but independent of M, the molecular weight of the polymer. The terms containing higher powers of $\mathbf{v}_2$ are usually negligible. This equation gives the activity of the solvent at a given composition of the solution if $\bar{V}_1/\bar{V}_2$ and μ are known.

Now

$$\bar{V}_1/\bar{V}_2 = V_1\mathrm{d}/M \tag{7}$$

(assuming the partial molar volumes to be equal to the molar volumes of the pure components), where V_1 is the molar volume of the solvent, and d is the density of the polymer, assumed to be independent of M. The quantity $\bar{V}_1/\bar{V}_2$ is therefore a measure of the molecular weight of the polymer, and Huggins' equation (equation 6) should give us information, regarding the dependence of solubility (expressed as $\mathbf{v}_2$) on molecular weight, necessary to the understanding of fractionation.

The constant μ is of no less importance, for its value depends on the liquid used with a given polymer, and will therefore vary as the composition of the binary mixture is changed during fractionation. Huggins has discussed in some detail (127) the factors that might be expected to affect the value μ: heat of mixing, the flexibility of the chain molecule, the molecular weight of the polymer, the concentration of the solution, the temperature, etc. Like Gee (100, 104), he relates the heat of mixing, which is an important factor in determining μ, to the "cohesive energy densities" of the polymer and the liquid (where cohesive energy density is, following Hildebrand (4), defined as the ratio of the molar latent heat of vaporization at constant volume to the molar volume), the heat of mixing being larger the greater the difference between these cohesive energy densities (100). If the difference is very great, the entropy of mixing is also affected, for then perfect randomness of mixing can no longer obtain. The result is that the entropy of mixing will be smaller than otherwise expected and the value of μ correspondingly larger.[8]

The effect on the entropy of mixing, and therefore on μ, of variation in flexibility of the chains is very slight; "a large decrease in flexibility makes μ slightly smaller in magnitude, if positive, or larger, if negative" (127). The contributions of both the heat and the entropy of mixing to μ should be smaller at higher temperatures because of the increasing probability of perfect mixing and the increasing flexibility of the chain molecules. In practice, μ is found to vary with temperature according to the equation

---

[8] The intrinsic viscosity $[\eta]$ of a polymer in a "poor" solvent (that is, one in which the heat of mixing is large) is less than that in a "good" solvent, a fact explained by assuming that the polymer molecules are more tightly coiled in the poor solvent (26, 89, 126).

$$\mu = \alpha + \beta/T \tag{8}$$

where α and β are constants. (This dependence of μ on temperature is the basis of another method of fractionation, for we can obviously increase μ, and thereby

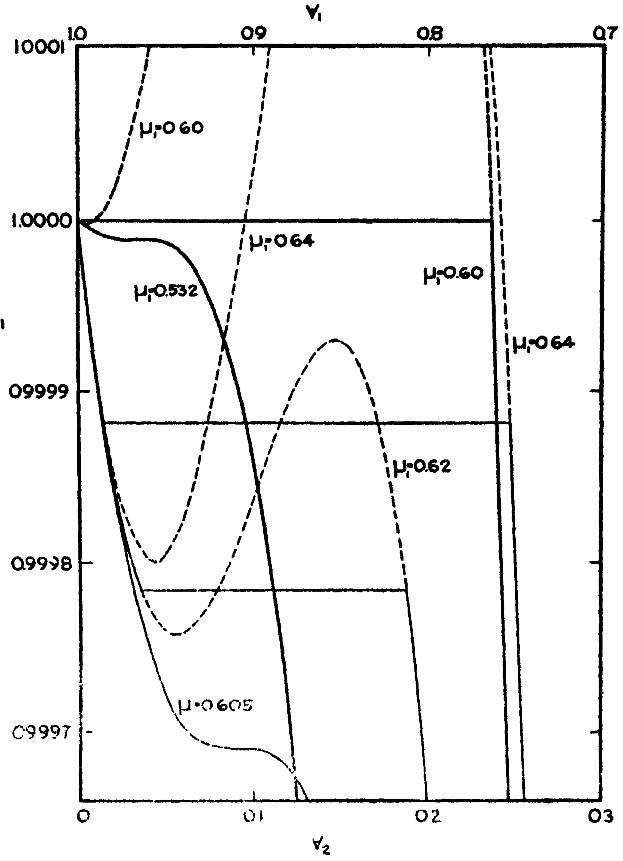

FIG. 1. Activity (a_1) vs. volume fraction for $\bar{V}_2/\bar{V}_1 = 100$ (lighter lines) and 1000 (heavier lines) at different values of μ (or μ_1). (From Huggins (5, p. 903)).

effect separation into two phases, by cooling as well as by addition of non-solvent.) μ is found to be almost independent of the molecular weight of the polymer and of the concentration of polymer in the solution (for a few systems it increases at high concentrations, but for the rubber–benzene system, for example, it is constant over the entire concentration range (127)).

The significance of μ for fractionation is probably best demonstrated by plotting the activity, a_1, against the volume fraction v_2 for various values of μ, keeping M constant (5, 127) (see figure 1). It is seen that when μ is below a critical value, the plot is a smoothly descending curve, and the polymer of this particular molecular weight is completely miscible in all proportions with the liquid; but when μ exceeds this critical value the curve shows a maximum and a minimum, indicating the presence of two phases. The shape of these curves shows that, in the region of partial miscibility, the liquid is much more soluble in the polymer than the polymer is in the liquid; one phase (the supernatant liquid) is almost pure solvent, while the other (the precipitated phase) is a more or less swollen polymer. The critical value of μ depends on M, as follows:

$$\mu_c = \tfrac{1}{2}(1 + \sqrt{\bar{V}_1/\bar{V}_2})^2 \tag{9}$$

so that as M becomes very large, μ_c approaches the value 0.5. Since in the high-molecular-weight range the values of μ_c are therefore very close together, fractionation will become correspondingly more difficult, and overlapping of molecular weights in the fractions more serious, in this range; this is the same conclusion as was reached by Mark (7) on the basis of a different theory, and it is in accordance with observed behavior.[9]

Gee (99) treated the problem of the solubility of a polymer (rubber) in a liquid in a similar way, except that in place of equation 4 he used a more complex expression for the heat of mixing. From his analysis it may be concluded (*1*) that for any liquid–polymer system there is a critical temperature above which complete miscibility obtains, this temperature being nearly independent of the molecular weight of rubber unless this be small; (*2*) that in the range of partial miscibility the concentration of polymer in the supernatant phase increases very rapidly with temperature (so that the temperature range in which a solubility is measurable is narrow), the coefficient increasing somewhat with temperature; and (*3*) that the composition of the precipitated phase depends only slightly on the molecular weight of the polymer.

In applying these theories to the fractionation of a heterogeneous polymeric substance, one should consider the possible effects on the solubility of a given polymer species of the presence in the same solution of other polymer species differing only slightly in molecular weight. Gee (99, 100), recognizing this need, used for the heat of mixing of such a polymeric substance an empirical extension of Flory's (89) equation for the entropy of mixing of long and short molecules (polymer and solvent), in the form

$$\Delta S_{\text{mix}} = -k(n_0 \ln \mathbf{V}_0 + \Sigma n_i \ln \mathbf{V}_i) \tag{10}$$

(where n_0 is the number of solvent molecules, n_i is the number of molecules of polymer species i, $\mathbf{V}_0$ and $\mathbf{V}_i$ are volume fractions, and k is the Boltzmann constant); and with this expression derived an equation relating the distribution of the two species i and j between the two phases. His analysis led to the conclusions that fractionation is more efficient the more dilute the solution and that no single-stage fractionation by any solubility method can give anything approaching complete separation. The first of these conclusions had already been reached by Schulz (246, 247, 253); both are borne out in practice.

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[9] Implicit in this discussion is the assumption that the relations are still applicable when the (homogeneous) polymer is mixed with others in a heterogeneous polymeric substance. That this assumption is valid, provided the molecular weight of the homogeneous polymer is replaced by the number-average molecular weight of the heterogeneous material, has recently been demonstrated theoretically by Scott (J. Chem. Phys. **13**, 178–87 (1945)).

Flory (91, 92), in a much more thorough treatment of the problem, gave a theoretical derivation of equation 10 and from it derived expressions for the partial molal entropies and free energies of solvent and polymer. He pointed out that as a result of simplifying assumptions embodied in the theory the theoretical values of the entropies did not agree well with experimental values, especially in dilute solutions, but that the free-energy values calculated from them did agree well with experiment if μ, which occurs in the free-energy expressions, were considered a semi-empirical function. (Compare Huggins' discussion of the same function, above). Applying these equations to the problem of the fractionation of a heterogeneous polymer, Flory (92) developed an equation relating the "partition factor" α (which is defined as $\frac{1}{x}\ln(\mathbf{v}'_x/\mathbf{v}_x)$, where x is the degree of polymerization of molecular species x, and $\mathbf{v}'_x$ and $\mathbf{v}_x$ are the volume fractions of this species in the precipitated and supernatant phases, respectively) to μ, to the concentrations of (total) polymer in the two phases, and to the number-average molecular weights of the polymers in the two phases. He showed that the conditions of fractionation depend both on α, which governs the relative concentrations of a species in the two phases, and on r (the ratio of the volume of precipitated and supernatant phases), which affects the relative amounts. The nature of α is such that the concentration of any species, even that of lowest molecular weight, is greater in the precipitate than in the supernatant solution, although the concentrations become more nearly equal the lower the molecular weight. In order to reduce contamination of the precipitate with lower-molecular-weight material to a minimum, it is necessary that r be made very small, that is, that the volume of the supernatant solution be very large relative to that of the precipitate. The original solution should therefore be very dilute. This conclusion is in agreement with the familiar observation that fractionation is more efficient the more dilute the original solution. Flory was also able to show that the importance of using dilute solutions becomes greater as the molecular weight at which separation takes place increases.

The theory to this point has been developed on the assumption that the solvent is a simple liquid, or, if a binary solvent–non-solvent mixture, can be treated as one whose properties are intermediate between those of the solvent and the non-solvent. Gee (102) derived equations for the osmotic equilibrium between such a binary mixture and a ternary mixture of polymer and the liquid mixture, the two being separated by a membrane permeable to the two liquids but impermeable to the polymer, and then applied the equations to the solubility of linear polymer in mixed liquids. He was able to show that mixed liquids do not in general behave as simple liquids, that the larger the heat of mixing of two liquids the greater is the solvent power of the mixed liquid relative to that which would be expected if the properties of the two liquids were additive. He showed further how the solubility behavior of a polymer could be predicted "qualitatively from the cohesive energy densities of the three components, and semiquantitatively from the measured heats of mixing of the three binary mixtures." He also found that the distribution of the liquids between the two phases was unequal, the precipitate being richer in the better solvent.

It must be remembered that certain assumptions only approximately valid have been made in developing the theory of fractionation and that perfect agreement between theory and experiment can therefore not be expected (92, 99, 100). Nevertheless, the repeated experimental verification of many of the conclusions reached is evidence that the reasoning is basically sound. Further development of the theory is inevitable, and will undoubtedly throw further light on the process of fractionation.

The conclusions drawn from theory and supported by experiment have proven reliable guides in carrying out fractionation. In general it may be said that certain principles are well established. Fractionation is never completely efficient; the fractions obtained are never completely homogeneous with respect to molecular weight (72, 92, 149, 158, 263), although more nearly so than the original material. Refractionation improves the uniformity of the fractions, but only up to a certain point; there is no further significant improvement after the third fractionation (263). Better results are obtained by suitably recombining a large number of small fractions, if only a few are required, than by separating out the few larger fractions directly. The efficiency of a fractionation is greater the more dilute the supernatant solution (38, 176, 293),[10] and it is greater in the lower than in the high molecular-weight range (92, 127). This behavior is well shown by an isothermal ternary phase diagram (52, 92, 176, 263), such as is drawn in figure 2 for the generalized system: polymer–solvent–nonsolvent. In the diagram, which of course has no quantitative significance, the separation of the curves for the different molecular species is greater at low polymer concentration, and, at a given concentration, greater in the lower-molecular-weight range.

1. *Fractional precipitation*

Fractional precipitation procedures are those in which the heterogeneous polymer is completely dissolved in a suitable liquid and then partially "precipitated". The precipitated phase, which contains the high-molecular-weight fraction, and the supernatant solution are separated by decantation (with or without centrifuging); more of the polymer is then precipitated, and the procedure is repeated. There are two principal ways in which precipitation can be effected, and these will be considered separately: (*a*) by adding a precipitant isothermally; (*b*) by lowering the temperature, keeping the total composition constant. A combination of the two can, of course, be used.

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[10] See, however, the evidence to the contrary obtained in recent experiments by Morey and Tamblyn (J. Phys. Chem. **50**, 12–22 (1946)).

In an actual fractionation, the choice of solvent and precipitant is important. Relative solvent and precipitating powers can be determined by titrating a solution of the polymer in the solvent with the precipitant, the end point being indicated by the sudden appearance of opalescence or turbidity (25, 83, 138). Such a procedure is called a precipitation titration. The larger the amount of precipitant needed to reach the end point, the greater is the solvent power of the solvent (when one precipitant is used with a series of solvents), or the smaller is the precipitating power of the precipitant (when one solvent is used with a series of precipitants). The position of the end point depends on the polymer concentration (302), as an examination of the phase diagram (figure 2) shows. The results of a precipitation titration study are best summarized in such a phase diagram, and the diagram is a valuable help in carrying out fractionations.

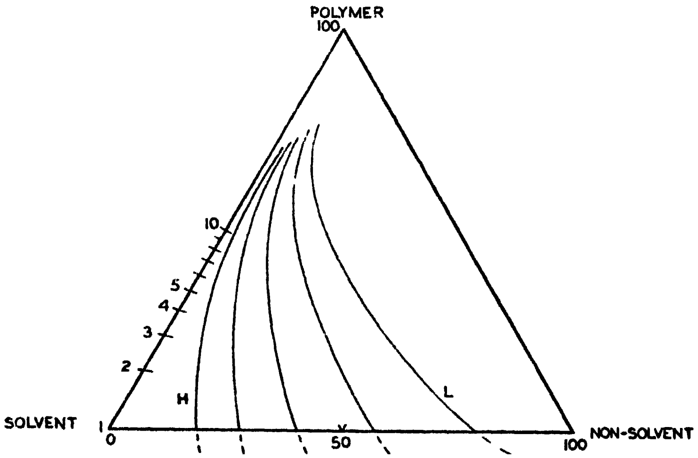

FIG. 2. General isothermal equilibrium diagram: polymer–solvent–non-solvent. H = highest molecular weight fraction; L = lowest molecular weight fraction. Adapted from H. Mark (Paper Trade J. **113**, 34–40 (1941)).

Theories as to why liquids differ in their solvent and precipitating power have not yet been completely formulated. Gee (103) showed that the solvent power of a binary liquid mixture is intermediate between that of the components only if they mix ideally; the larger the heat of mixing, the greater is the solvent power of the mixture relative to that of the components. Erbring (81) compared the precipitating power of the saturated monohydric alcohols from methyl to octyl (including some secondary ones) on the following systems: (*1*) polystyrene in each of ethyl acetate, butyl acetone, carbon tetrachloride, chloroform, methyl ethyl ketone, benzene, xylene, toluene, and monomeric styrene; (*2*) cellulose acetate in acetone; (*3*) paraffin in benzene; (*4*) rubber in each of benzene, carbon tetrachloride, and chloroform. In general, he found a relationship between precipitating power and dielectric molecular polarization of the alcohol; in (*2*) and in most cases in (*1*), there was a direct relationship; in (*3*) and (*4*) it was inverse; but with polystyrene in methyl ethyl ketone the precipitating power was virtually independent of the molecular polarization. Since the molecular polarization increases with the molecular weight of the alcohol, this means that the higher alcohols are more effective than the lower ones in precipitating cellulose acetate (which contains polar groups), but less effective in precipitating the non-polar substances paraffin and rubber. In later work, polystyrene (82), polyvinyl chloride (80), and polyisobutylene (80) were found to behave like paraffin and rubber in this respect. Polymethacrylic esters (80) behaved like cellulose acetate; with benzyl cellulose (80) a maximum precipitating power is shown by hexanol. Even more significant than its correlation with molecular polarization is the relationship of precipitating power to the quantity μ^2/ϵ where μ is here the dipole moment and ϵ the dielectric constant; this relationship is approximately linear in many cases (80, 82). Similar studies have been made by several other workers (105, 146, 175, 286, 303).

It is obvious that the end point of a precipitation titration may be located by observing the sudden increase in turbidity, either directly (138) or instrumentally (25, 83, 105, 195, 233). Gehman and Field (105), for example, observed that if light-scattering measurements are made as precipitant is slowly added, the intensity begins to increase long before two phases separate, but that there is a very marked increase of intensity at the precipitation point. They attributed the earlier increase in turbidity to aggregation of the molecules into loose clusters. The precipitation point may also be detected by measuring the depolarization of scattered light (105), the surface tension (174), or the viscosity, during the titration. Viscosity measurements, in particular, have frequently been used for this purpose (119, 153, 174, 224, 233). The marked decrease in the viscosity of a polymer solution on the addition of a non-solvent is a familiar phenomenon; several explanations for it have been advanced (105, 110, 276), but it is probably best explained as due to the tighter curling and more compact shape of the polymer molecules in the "poorer" solvent medium (26, 126). As more non-solvent is added the viscosity decreases less rapidly (105) (and may become constant (110) or even increase slightly (153)); the sudden decrease in viscosity when precipitation begins therefore produces a sharp break in the "viscometric titration" curve at the end point (see, for example, figure 3).

Precipitation titration can be used to determine the molecular weight of a polymer in a solution (the weight-average molecular weight in the case of a heterogeneous polymeric substance). This method, like that involving the determination of intrinsic viscosity, is a relative one, and must be calibrated using one of the absolute methods (ultracentrifuge, osmotic pressure, light scattering). The Schulz equation (equation 2), which is valid for a wide variety of polymeric substances, may be used for this purpose in the form $\lambda^* = A + B/\bar{M}$. It is obvious from this equation that the sensitivity of the method decreases with increasing molecular weight. This method was applied by Schulz and Dinglinger to polymethyl methacrylates (250), by Staudinger to polystyrene (274), by Jirgensons to degradation products of proteins (131–137), by Adams and Powers to varnish resins (25), by Baker, Fuller, and Heiss to ω-hydroxyundecanoic self-polyesters (30), by Husemann to degraded glycogen (129), and by Lovell and Hibbert to polyoxyethylene glycols (168). It is a promising new method, attractive because of its simplicity.

(a) Fractional precipitation by the addition of a precipitant

In this method fractionation is effected by adding to a solution of the polymer a suitable amount of precipitant, enough to cause separation into two phases, but not enough to cause precipitation of all the polymer present; the phases are then separated, and the procedure repeated with the supernatant liquid, until all the polymer has been precipitated (material of very low molecular weight may remain in solution even when excess precipitant has been added, but the amount is usually not large). In a preparative method, the fractions are recovered from the precipitated phase by evaporation of the solvent and drying; in an analytical method, it is usual to determine the amount of unprecipitated polymer in the supernatant liquid by evaporating an aliquot sample. Various modifications of these fundamental procedures are possible; these will be discussed as the individual fractionation procedures are considered.

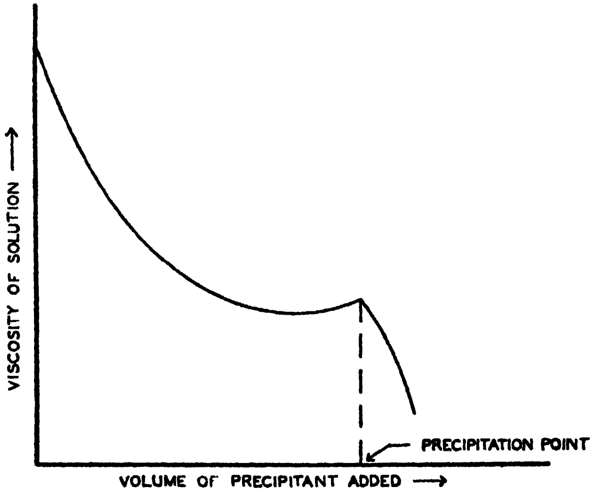

FIG. 3. A viscometric precipitation titration curve

(*1*) *Rubber and other natural hydrocarbons:* Caspari in 1913 (51), in a discussion of the fractionation of rubber into sol and gel by diffusion, expressed the opinion that a separation by fractional precipitation with alcohol or acetone would not be possible. Again in 1915 (52), on the basis of phase studies of the systems rubber–benzene–alcohol and rubber–benzene–acetone, he concluded that even if rubber were heterogeneous, fractional precipitation would not be feasible.

In spite of his conclusions, fractional precipitation was used successfully by Pummerer and Koch (218) in 1924 for the purpose of purification of rubber. These authors precipitated rubber from a 3 per cent solution in benzene by adding a 1:1 benzene–alcohol solution (in an atmosphere of carbon dioxide to exclude air and prevent degradation). They found that the impurities were removed with the first fraction. This procedure was further studied by Pummerer and Miedel in 1927 (219); it was found that when just enough precipitant was added to produce permanent turbidity, the first fraction contained 30–40 per cent of the total rubber hydrocarbon, together with all the impurities. The material remaining in solution was considered pure, since its elementary analysis corresponded to the theoretical formula. A study was also made of other solvents (hexahydrotoluene, petroleum ether, ethyl ether) and other precipitants (acetone) for use in the process. The best control of the conditions of precipitation was achieved with petroleum ether as solvent and acetone as precipitant. In some cases there was some doubt about the purity of the product, for traces of nitrogen were found to be still present. In 1928 the same authors (220) critically compared the various purification procedures in use at that time. The fractional precipitation technique was improved by repeating the precipitation and by varying the solvents, precipitants, concentration, and temperature; in the hope of achieving a more thorough purification, a different solvent–precipitant system was used in each refractionation. Eight fractions were obtained in this way, but the authors were still not satisfied with the purity of their products.

In 1939 Kovarskaya and Lipatov (147) fractionated pale crepe rubber by precipitation with ethanol from solution in either ethyl ether or benzene; six fractions were obtained, and used in a viscosity study.

In 1941, Kemp and Peters (141) compared various fractionation methods: diffusion into a single solvent, solution in mixed solvents of varying composition, precipitation by cooling, and finally a combined diffusion and precipitation method. This last procedure, which they considered the best, was as follows: 2.5 g. of finely cut crepe rubber was left to diffuse into 500 cc. of chloroform for definite periods of time at 25°C., and the resulting solution then fractionally precipitated with methanol. The residue was covered with 500 cc. of fresh chloroform, and the procedure repeated three times. Throughout, the work was carried out under an atmosphere of nitrogen. The separation was good, and no breakdown occurred.

In 1930, Staudinger (280) reported a fractional precipitation procedure for hydrorubber, a derivative of rubber produced by complete hydrogenation. He obtained five fractions by precipitating the ether solutions with alcohol.

(*2*) *Cellulose nitrate:* A great deal of work has been done on the fractionation of the cellulose esters, especially the nitrates and the acetates. This is not only because the esters themselves are of great industrial importance, but also because the best way to determine the distribution of cellulose itself is to nitrate or acetylate it carefully under such conditions that breakdown is minimized, and then fractionate the esters. The fractionation of cellulose itself has been carried out, and examples will be given later; but it presents considerable difficulties for cellulose does not dissolve in any simple solvent, and any liquid that does act as a solvent usually causes some breakdown (15).

The first paper to be published on fractional precipitation dealt with nitrocellulose; in it, Duclaux and Wollman (74), in 1920, introduced the method, which is still the standard and most widely used one, of precipitating an acetone solution with water, or with a water–acetone solution. One hundred and ten grams of commercial nitrocellulose was dissolved in 2 liters of acetone; with continual stirring, 1400 cc. of an acetone–water solution (60 per cent acetone by volume) was added; this gave, after separation and evaporation, the first fraction (42 g.). To the supernatant liquid 1 liter of 20 per cent acetone solution was added, and a second fraction (47 g.) precipitated. Then an excess of water was added, and the third fraction (16 g.) was obtained. Each of the fractions was fractionated in turn, but found to be still heterogeneous. By comparing properties of the fractions, it was found that they differed in viscosity (and therefore in molecular weight), but not in nitrogen content.

This method was adapted by Bréguet (41) in 1925 for use with celluloid, by using benzene as the precipitant instead of water in order to prevent the precipitation of the camphor.

In 1928, Kumichel (153) first described the technique of locating the precipitation point viscometrically. He found that on adding a 1:1 acetone–water solution to an acetone solution of nitrocellulose, the viscosity first fell, then increased again to a sharp point, at which turbidity appeared; a few more drops made the viscosity fall to a very low value, and precipitation occurred (see figure 3). After separation, two fractions were obtained by drying the precipitate and ultrafiltering the supernatant liquid. By a repetition of this procedure, the uniformity of the fractions could be improved.

Duclaux and Nodzu (73) in 1929 compared fractional precipitation with other fractionation methods involving diffusion and ultrafiltration. The earlier finding, that the fractions differ in molecular weight but not in the degree of nitration, was confirmed.

In 1930, Beck, Clément, and Rivière (35) carried out a fractional precipitation of a 16 per cent acetone solution of nitrocellulose by adding varying amounts of a 20 per cent water–80 per cent acetone mixture. As the last (fourth) fraction could not be precipitated with water, a barium chloride solution was used, but difficulty was experienced in washing out the barium chloride afterwards without peptizing the precipitate. A rather ingenious continuous procedure was described: a mixture of nitrocellulose, acetone, and water, in proportions such that precipitation did not occur, was distilled at reduced pressure at room temperature; as the acetone evaporated more rapidly than the water, a composition was soon reached at which precipitation began, and thereafter precipitation proceeded as the distillation continued. This method gave eleven fractions.

Duclaux and Barbière (72) in 1933 showed by successive fractionations that there is a limit beyond which the uniformity of a fraction cannot be significantly improved by further refractionation.

In 1933, Medvedev (182, 183) fractionated nitrocellulose, using acetone as the solvent and water as the precipitant. He introduced the practice of determining the amount of precipitant to be added by carrying out a preliminary titration of a small sample. He obtained nine fractions by suitable refractionations and compared their characteristics.

In 1934 and 1935, Glikman (Glückmann) (107, 108, 109, 111, 112) used Duclaux's fractional precipitation method in his study of the nature of nitrocellulose solutions. In some cases (109) solvents other than acetone were used (ethyl acetate, benzene). A fractionation by vacuum and ordinary distillation of a nitrocellulose–acetone–water mixture was also attempted (111). The fraction used by Dobry (63, 64) in her work on the viscosity and the osmotic pressure of nitrocellulose was obtained by precipitation, probably by Duclaux's method.

In 1935, Rogovin and Glazman (225) used the method to separate commercial nitrocellulose into three fractions, but unlike other investigators, they found a lower nitrogen content in the lowest fraction.

Schulz (243) in 1936 used a similar method but, realizing the importance of temperature control, carried out the separation after long standing (1–2 days) in the thermostat at 27°C.

Spurlin (264) in 1938 rejected water as a precipitant, because it produces a high Tyndall effect. Instead he used acetone as the solvent, with heptane as the precipitant. Six fractions were obtained in the first fractionation; fractions of approximately the same viscosity were combined, and refractionated. This was repeated twice, giving a total of sixty-six fractions, which were combined to give seventeen. A high degree of separation was attained, but not homogeneity. This is an important study, because of the large number of fractions and their relative uniformity; it made possible a valuable study of the correlation of mechanical properties with molecular weight.

Rath and Dolmetsch (223) in 1938, in a search for the best method of determining the heterogeneity of cellulose, tried among other things a fractional precipitation of the nitrated product from acetone solution with water or ethanol. Similarly, Staudinger and Jurisch (278), in 1939, fractionated cellulose nitrate by precipitation with water from solution in acetone.

In 1940, Jurisch (138) precipitated cellulose nitrate from acetone by titrating with water. He described carefully the appearance of the solution near the precipitation point, as this is somewhat difficult to recognize. The mixture was then centrifuged, and the supernatant solution decanted. The precipitate was washed out of the centrifuge tube with acetone, reprecipitated with methanol and water, dried, and weighed. Although some material was lost in this process, this was not considered important, for the loss did not come from any one fraction, and the results were therefore not distorted.

Schulz (252, 254) fractionated nitrocellulose in 1941 and 1942, but did not describe his method.

(3) *Cellulose acetate:* In his study of the viscosity of cellulose acetate solutions, in 1923, Mardles (172) mentioned that the fractions he used were obtained by precipitation with water from acetone solution, but gave no further details.

In 1928, Caille (46) described a fractionation procedure as follows: 10 g. of cellulose acetate was dissolved in 300 cc. of acetone, 100 ml. of acetone-water (1:1) solution was added with stirring, and the precipitate was washed and dried; the process was then repeated on the supernatant liquid.

McNally and Godbout (171) in 1929 precipitated a 10 per cent acetone solution fractionally with 3:1 water–acetone solution; the separation of phases was carried out by centrifuging.

In 1930 Rocha (224) applied the "viscometric titration" method of Kumichel to cellulose acetate. He obtained three fractions, the lowest of which contained most of the impurities, and characterized them very thoroughly by various chemical and physical tests. The fractional precipitation of cellulose acetate from acetone with water is often known as Rocha's method, although he did not originate it.

Ohl in 1930 (205) and 1932 (206) applied the same method and obtained three fractions, of which the second was the purest. A correlation was found between properties of fractions and the quality of products made from them; therefore, fractionation was suggested as a basis for judging the quality of cellulose acetate. The method was also used in 1931 by both Iwasaki (130) and Caille (47).

Herzog and Deripasko (119) in 1932 made a study of other solvent–precipitant systems for use in the fractionation of cellulose acetate; among them methyl glycol–water and acetone–petroleum ether. The precipitation point was determined viscometrically as by Rocha.

In 1934, a whole series of papers was published. Clément and Rivière (53), Obogi and Broda (203), and Herz (117) all used methods similar to those already described. Elöd and Schmid-Bielenberg (77) and Hess and Ulmann (120) used chloroform as the solvent and methanol as the precipitant. In 1935 Rocha's method was used by Ulmann (293), who emphasized that the solution should be dilute, but considered the 2.5 per cent solution he used dilute enough.

An important series of studies was made in 1937–39 by Lachs, Kronman, and Wajs (155, 156, 157, 158, 159). Their object was to find a method for determining the molecular-size distribution of cellulose; for that purpose, they acetylated it, and then precipitated the cellulose acetate fractionally from the final reaction mixture (1:1 acetic acid–acetone) with water. Usually four fractions were obtained. The general shape of the precipitation curve was noted: at first, the addition of large amounts of water produced little precipitate, then the further addition of small amounts caused heavy precipitation, and then the curve levelled off again, until no more precipitate could be obtained although some low-molecular-weight material was left in solution. It was confirmed that the fractions had the same acetyl content, but different viscosities. By successive acetylation, saponification, and reacetylation it was shown that little breakdown occurs in the process of acetylation. Cellulose from five different sources was used for this work. The degree of heterogeneity was measured roughly by the difference in viscosity of the first and last fractions. A second fractionation of the above fractions was then carried out, by precipitation with methanol from chloroform solution. It was shown that the first fractions were not homogeneous, but the estimate of the heterogeneity of the original cellulose was not greatly affected. An artificial mixture of two different fractions was fractionated, to prove the efficiency of the method.

In 1938, Levi *et al.* (164) used this method, with benzene as precipitant and acetone as solvent, as a standard against which to compare a fractionation (of cellulose acetate) by chromatographic adsorption.

Danilov *et al.* (59) in 1939 used fractional precipitation from acetone solution with ethyl ether as a means of purifying cellulose acetate. In the same year, Bezzi and Croatto (37) used a fractional precipitation involving the addition of water to an acetic acid solution. Mark and Simha (180) in 1940 applied Rocha's method on a larger scale, using 4 kg. of cellulose acetate.

A careful study of the fractional precipitation of cellulose acetate from acetone solution with ethanol was made by Sookne, Rutherford, Mark, and Harris (263) in 1942. To 150 liters of a 2.5 per cent solution of commercial cellulose acetate a quantity of ethanol insufficient to produce precipitation at room temperature was added, and the mixture cooled slowly to 10°C., where precipitation occurred. The phases were separated by decantation and the procedure repeated. The amount of ethanol to be added was determined in each case by a preliminary test-tube experiment. Three fractionations were done, fractions of closely similar mean-degree of polymerization being combined after each step; finally, fifteen fractions were obtained. The distribution curves plotted after each step show that refractionation results in improvement, but that no more improvement is possible after the third fractionation, although the fractions are still not homogeneous. These fractions were used in 1943 by Bartovics and Mark (31) in an osmometric and viscometric study.

(4) Cellulose ethers and other derivatives: Okamura (207) in 1933 fractionated technical ethyl cellulose by precipitation with water from glacial acetic acid solution. This solvent caused some breakdown, but not enough to matter.

Glikman (Glückmann) (110, 113) in 1936 and 1937 prepared fractions of benzyl cellulose, by precipitation with alcohol from an alcohol–benzene solution; they differed in molecular weight, but not in the degree of etherification. He also studied the temperature dependence of the precipitation, and the changes in the viscosity on addition of precipitant.

Signer and Liechti (259) in 1938 used a somewhat different method of fractionating a water-soluble methyl cellulose. To a 2.5 per cent aqueous solution of the technical material saturated sodium sulfate solution was added, and after separation of the precipitated phase the supernatant liquid was treated with solid sodium sulfate; fractions III and IV were also obtained with the use of the solid salt. (This "salting out" procedure is somewhat different in principle from the methods which use two liquids.) Fraction IV was refractionated, this time with acetone as the precipitant. The fractions had to be freed from sodium sulfate by dialysis or electrodialysis. Fractions differed not only in molecular weight, but also in methoxyl content.

Staudinger and Reinecke (279) in 1938 fractionated ethyl cellulose by precipitation with water from dioxane solution, obtaining three fractions of identical chemical composition.

In 1939 Ushakov *et al.* (294) described another method for fractionating ethyl cellulose, involving precipitation with gasoline from a 4 per cent alcohol solution.

They found that, in many cases, the fractions differed chemically as well as in molecular weight. The mechanical properties of the films obtained from the fractions were compared.

Fink, Stahn, and Matthes (85) in 1934 fractionated cellulose xanthogenate (viscose) by precipitation with methanol or ether from an aqueous pyridine solution. The fractions differed chemically as well as in chain length.

(*5*) *Cellulose:* As mentioned above, the direct fractionation of cellulose presents considerable difficulty (15), for cellulose does not dissolve in any simple solvent; the usual solvents, such as sodium hydroxide, phosphoric acid, or cuprammonium (Schweizer's reagent), all dissolve cellulose by chemical action, which is often drastic enough to cause appreciable breakdown, thus invalidating the results. Attempts have been made, however, to use all of these solvents, as well as others, for fractionation; for, in the more usual alternative procedures of nitrating or acetylating the cellulose and then fractionating, breakdown also occurs, during the esterification process. The choice is therefore one of two evils.[11]

In 1939, Tydén (291) brought cellulose into solution by digestion with zinc oxide and sodium hydroxide, and then precipitated it fractionally by "salting out" with sodium sulfate. It was found better to add the sodium sulfate in two portions, with a 3-hr. interval between additions, in order to obtain a smaller fraction; even then, 66 per cent of the cellulose precipitated. The concentration of the cellulose was about 0.1 per cent, and that of sodium sulfate 7–15 per cent; 12 hr. was required for complete flocculation. In this process, breakdown was minimized, but nevertheless did occur.

In 1942, Strauss and Levy (284) claimed that fractionation procedures for cellulose could be considerably improved by using their new solvent, cupriethylenediamine, which they had previously used successfully for viscosity measurements on cellulose; solutions of cellulose in this solvent are said to be less sensitive to breakdown than in others, especially by atmospheric oxygen. Cellulose, dissolved in 0.5 molar cupriethylenediamine solution to give a 1 per cent solution, was precipitated by titrating with 8 *N* sulfuric acid, with stirring, at 25°C.; the fractions were separated by centrifuging and decanting. Eight fractions were obtained by this procedure.

Further studies of fractional precipitation of cellulose were made in 1943 by Coppick, Battista, and Lytton (55). They decided in favor of an analytical rather than a preparative procedure, as this requires less time and less handling of the material, and thus minimizes degradation. In the actual method used, sodium hydroxide was the solvent, aqueous acetone the precipitant. In order to effect complete solution of the cellulose in the sodium hydroxide, the mixture was cooled slowly in an acetone–solid carbon dioxide bath with gentle stirring until solidification took place; then with vigorous stirring it was warmed up to

[11] Indeed, for the fractionation of cellulose, a solution method is often preferable to precipitation, because it does not require the preliminary complete solution of the whole sample, a step which is sometimes impossible and often difficult, and which usually requires long periods of contact with the solvent, thereby increasing the chances for breakdown.

room temperature and the required quantity of aqueous acetone was added to it dropwise over a period of half an hour. The precipitate was separated by centrifuging and discarded. The amount of unprecipitated cellulose was then determined by adding acetic acid and methanol to an aliquot portion of the supernatant liquid at 0°C. until precipitation was complete, followed by washing, drying, and weighing the solid. Its cuprammonium viscosity was then determined to find the chain length needed for plotting the distribution curve. To obtain other fractions, the same amounts of different precipitation mixtures (20–50 per cent by volume of acetone) were added to fresh portions of the solution. (This is a typical analytical procedure; the fractions are never isolated at all, for the precipitates are discarded; the information obtained,—namely, the concentration of polymer remaining in solution after a known amount of precipitant has been added, and the viscosity of this polymer,—is sufficient to obtain a distribution curve, which is all that is required.) This method, useful for rayon, was adapted for use with wood pulp and cotton linters, which are only slightly soluble in sodium hydroxide. A special pretreatment, involving reprecipitation from cupriethylenediamine, was necessary to bring about complete solution in sodium hydroxide (6 *N*). Otherwise the procedure was similar.

(*6*) *Natural products other than rubber and cellulose:* Most of the proteins are neither linear in structure, nor heterogeneous in molecular weight (as Svedberg has shown with the ultracentrifuge). In this account, we are interested only in linear heterogeneous proteins, capable of forming a homologous polymeric series. Such a protein is gelatin. In 1926, Northrop and Kunitz (202) separated gelatin into two fractions by precipitation with alcohol from water, and compared the properties of the fractions. Nagorny (199) in 1927 accomplished the same end by fractional salting out with ammonium sulfate.

Among the carbohydrates other than cellulose, glycogen and starch have received some attention. Staudinger and Husemann (277) in 1937 fractionated glycogen by precipitation with methanol from formamide solution; comparative osmotic and viscosity measurements indicated, however, that the molecules are spherical rather than linear. In 1941, Husemann (129) used fractional precipitation to purify hydrolytically degraded glycogen; he separated it into three fractions by precipitation with methanol from 0.1 *N* calcium chloride solution, and discarded the first and last fractons. Levine, Foster, and Hixon (165) in 1942 applied a fractional precipitation procedure to crude dextrins obtained from corn syrup, precipitating with methanol from water solution; the fractions contained only from two to twenty-six glucose units per molecule, and were therefore not truly high-molecular.

Coppick and Jahn (56) in 1943 made a study of nitrated wood, and described a procedure for fractionating nitrated spruce mechanical pulp by slow precipitation from acetone with alcohol and water. Eight fractions were obtained.

(*7*) *Synthetic products:* Synthetic high polymers have increased remarkably in importance in the last few years; most of the fractionations reported are therefore comparatively recent. Nevertheless, Staudinger some time ago used synthetic polymers, such as polyethylene oxides and polystyrenes, as models in trying to elucidate the structure of the natural high polymers, and some early fractionation methods are due to him. In 1927 he (275) reported two methods for the fractionation of polyvinyl acetate, one by fractional solution, another by fractional precipitation; in the latter the addition of petroleum ether to a rather concentrated (40 per cent) benzene solution yielded three fractions. In 1929 he (273) reported a fractionation of polystyrene that is of special interest, because the precipitation was effected by an excess of solvent. The method was applied to the hemicolloidal (relatively low molecular weight) polystyrene: 170 g. of polymer was dissolved in 500 cc. of acetone; when 1000 cc. more of acetone was added, part of the polymer precipitated as a thick liquid. The process was repeated, and the last fraction, after partial evaporation of the acetone, was obtained by precipitation with alcohol. A refractionation from benzene solution was effected by the addition of a solution of benzene in alcohol. Five fractions were obtained in this way. In the same year, Staudinger and Schweitzer (281) obtained three fractions by the precipitation of polyethylene oxide with ether from benzene solution.

In 1928, Whitby and Katz (300) studied the polymerization of indene, cinnamalfluorene, and cinnamalindene. They demonstrated the heterogeneity of the products by fractional precipitation, using benzene as the solvent and alcohol as the precipitant; polyindene yielded seven fractions, polycinnamalfluorene five, and polycinnamalindene four. The same authors (299) reported another fractionation of polyindene in 1930, involving precipitation with alcohol from chloroform solution. Three fractions were obtained as follows: to a solution containing 450 g. of polyindene in 1200 cc. of chloroform, 200 cc. of alcohol was added dropwise with stirring. After separation of the first fraction, 1 liter of alcohol was added to the supernatant liquid to give the second fraction. The third fraction was obtained by concentrating the second supernatant liquid to 200 cc. The first fraction was subjected to nine refractionations, to remove the low-molecular-weight polymer.

In 1930, Whitby (297) described a fractional precipitation of polystyrene from benzene solution (1.5 per cent) with ethanol; three fractions were obtained. He also gave the results of a fractionation of polymerized dimethylbutadiene, without describing the method. In 1932 he (298) mentioned a similar fractionation of polystyrene in which he obtained six fractions.

A careful study of the fractionation of polystyrene, the most widely studied synthetic polymer, was made in 1934 by Daneš (58). He emphasized the temperature dependence of solubility, and the importance of close temperature control; he also used dilute solutions, to prevent the formation of emulsions, which are difficult to break. He employed the very useful technique of heating the mixture (after addition of precipitant) to not more than 20° above thermostat temperature until it formed a clear solution, and then letting it cool slowly, thereby ensuring conditions more favorable for the maintenance of equilibrium, and improving the homogeneity of the fractions. His solvent was benzene; his precipitant a mixture of methanol and acetone. Some of the fractions were refractionated.

Schulz and Husemann (251) in 1936 also fractionated polystyrene, using methyl ethyl ketone as the solvent and methanol as the precipitant. Temperature control was used, and seven fractions were obtained. In the same year, Dobry and Schwob (67) fractionated polystyrene by precipitation with methanol from various solvents: chloroform, benzene, tetralin, carbon disulfide, carbon tetrachloride, dioxane, pyridine. Two fractions only were obtained, for osmometric and viscometric study.

In 1936, Komarov and Selivanova (146) studied the conditions of the precipitation of sodium butadiene polymers from benzene solution by means of various alcohols and other liquids. They found that decrease in concentration and increase in temperature result in an increase in the amount of precipitant required. The chemical nature of the precipitant has a great influence on the position of the precipitation point; the series, in order of decreasing precipitating power, is: methanol, ethanol, phenol, propanol, acetone.

In 1936, Douglas and Stoops (71) used an analytical fractionation method to determine the distribution in vinyl ester resins. Measured amounts of precipitant (acetone–water solution) were added to a solution of the resin in acetone; a determination of total solid was made on a 10-cc. aliquot portion of the supernatant liquid; then, without separating the precipitate, more precipitant was added, and the procedure repeated. The considerable error was due to the overlapping of the molecular-weight ranges of the fractions.

Zhukov and Komarov (305) in 1938 reported the separation of sodium bivinyl polymer, by precipitation with alcohol from benzene solution, into four fractions. In the same paper an analytical procedure was also described in which varying amounts of alcohol were added to three portions of a 1 per cent benzene solution, and the precipitated fractions weighed.

In 1941, Schulz and Dinglinger (250) fractionated polymethyl methacrylates by successive additions of cyclohexane to benzene solutions. Blease and Tuckett (38) precipitated polyvinyl acetate from solution in acetone with 1:1 methanol–water solution; water was the actual precipitant, methanol acting merely as a diluent, to ensure easier control of the precipitation point; the control was also improved by precipitating at a higher temperature, because the quantity of precipitant to be added is then larger. It was found that a better separation was obtained in more dilute solution.

In the same year, Fuoss (95) described a procedure for the fractionation of polyvinyl chloride, using mesityl oxide as the solvent for low-molecular-weight products, cyclohexanone for high-molecular-weight products, acetone as a diluent, and methanol as the precipitant. Two methods were given, differing mainly in the quantities of materials used. The smaller-scale method (used more for analytical than for preparative purposes, although the fractions were actually separated) was as follows: 1 to 2 g. of polymer in a tared 200-cc. centrifuge bottle was moistened with acetone (for dilution improves the fractionation). Methanol was then added from a weight buret through a capillary funnel, in such a way that it mixed with acetone at indentations in the condenser, and was thus diluted without increasing the total volume of the solution. The solution was cooled slowly, then chilled in ice, and centrifuged; the supernatant liquid was decanted into another tared centrifuge bottle, and the procedure repeated. The precipitates were coagulated, filtered, dried, and weighed, and samples taken for viscosity determinations. In 1943, Fuoss and Mead (96) prepared polyvinyl chloride fractions by precipitating an acetone extract of the polymer with methanol.

In 1942, Staudinger *et al.* (270) reported a fractionation of polyisobutylene. The hemicolloidal products were precipitated with acetone from benzene solution, the mesocolloidal and eucolloidal products with acetone or methanol from toluene solution. Kern and Fernow (145) fractionated polymethacrylonitrile in 1942 by precipitation with methanol from a 1 per cent solution in acetone.

In 1943, Flory (90) fractionated polyisobutylene and used the fractions in a comparative viscosity–osmotic pressure study. He precipitated a 1 per cent benzene solution with acetone, added in slight excess of the amount required to produce incipient cloudiness. The mixtures were then warmed until they became homogeneous, and cooled slowly until the phases separated again. The precipitates were reprecipitated several times with acetone from benzene, in order to purify them. It was shown conclusively that degradation did not occur in this procedure. This is a very thorough and important study.

In the same year, Alfrey, Bartovics, and Mark (27) fractionated polystyrene, also for osmotic-pressure and viscosity measurements. A 2 per cent solution in methyl ethyl ketone was titrated with methanol until cloudiness appeared, and warming and slow cooling was used, as by Flory, to ensure equilibrium conditions during precipitation. The fractions were purified by reprecipitation with methanol from toluene solution, and subjected to two consecutive refractionations; the total number of fractions obtained was twenty.

Kunc and Miller (310) in 1941 patented a method of fractionally precipitating isoölefin polymers from solution in hydrocarbon and other non-polar solvents by aliphatic oxygen-containing precipitants; as examples they described the precipitation of polyisobutylene from benzene with acetone, and from carbon disulfide with ethyl ether.

Kemp and Straitiff (144) in 1944 fractionated Buna S by precipitating a 2 per cent benzene solution with methanol. This was done by adding a 1:1 methanol–benzene solution slowly with vigorous stirring until cloudiness appeared, and separating the supernatant liquid from the precipitate by decantation at 20°C. The authors concluded from their results that the distribution of Buna S is too broad, resulting in poor processing characteristics.

(b) Fractional precipitation by cooling

It has been pointed out many times (27, 58, 90, 243, 251) that the precipitation point of a polymer–solvent–precipitant system depends very markedly on the temperature; rather careful control of temperature during a fractional precipitation is therefore necessary, a fact that many authors have failed to realize. This temperature dependence of solubility (and of the partition coefficient of each molecular species of the polymer) can be and has been used in carrying out fractionations; in fact, Mark (176) maintains that a better resolution can be obtained in this way than by the more usual methods just described. The process is somewhat analogous to fractional crystallization in low-molecular chemistry, but the precipitates are not usually crystalline.

In 1929, a process was described (308) by which cellulose acetate could be fractionated by cooling a solution in a mixture of benzene and methanol or ethanol; it was claimed that the higher fractions give filaments, films, lacquers, and other commercially valuable products, with properties superior to those of similar products made from the unfractionated material.

Staudinger and Bondy (271) in 1930 found that balata, a naturally occurring geometrical isomer of rubber, could be fractionated[12] by cooling a warm solution in benzene, toluene, or xylene. In the method described, 17 g. of balata was dissolved in 500 cc. of xylene at 25°C., cooled to 10°C. with constant stirring, and allowed to stand for 24 hr. at that temperature; the mixture was then separated by centrifugation and decantation. This procedure was repeated until the last portion had to be separated by precipitation with a methanol–acetone mixture; this was fraction I. The other fractions were obtained by repeating the procedure on the combined precipitates. Five fractions were prepared in this way.

Scheidegger (311) in 1934 used fractional precipitation by cooling to purify cellulose acetate; benzene–ethanol or benzene–methanol mixtures were the solvents. He claimed that the precipitated fraction decomposed at a higher temperature, and gave less brittle films, than the original material.

By far the most important work[13] in this field has been done on natural rubber by Midgley and his associates (186–193) in the period 1931–42. Their method (186, 187, 189) was based on precipitation from solution by slow cooling. Crepe rubber and benzene were heated together to 50°C., and a solution of (absolute) alcohol and benzene was added slowly, with stirring, until the rubber was completely dissolved. The solution was then cooled slowly to a temperature 1°C. below that at which turbidity is first observed (the precipitation point) and kept at that temperature for 1 hr. The two phases that formed (supernatant and "gel") were separated by decantation. From the supernatant phase a rubber fraction was recovered by chilling in an ice bath; the resulting mother liquor was warmed and the "gel" phase dissolved in it by warming and stirring. These steps were repeated three times, yielding altogether four fractions, A_1, A_2, A_3, and A_4. When an attempt was made to obtain a fifth in the same way, the precipitate did not completely dissolve even at the boiling point of the mixture. From the supernatant liquid a fraction A_5 was obtained, and from the residue (by extraction with benzene in a Soxhlet apparatus) a soluble fraction A_6, and an insoluble fraction B. As the purpose of the process was to effect a purification, and as most of the impurities were in the B and other high fractions, the first three fractions only were refractionated until nitrogen-free rubber was obtained. Later (190) the importance of preventing degradation by oxygen and light was realized, and the precautions were taken of excluding light and working in a vacuum or in an atmosphere of carbon dioxide. It was found that there was little advantage in refractionating more than twice, as the product of the third fractionation was only slightly better than that of the second. The fractions were characterized by determining the "standard precipitation point", or s.p.p. (190), that is, the temperature at which a sudden increase in turbidity appears in a slowly cooled solution of standard composition. From this study it was concluded that 50 per cent or more of the purified rubber (rubber hydrocarbon) is one soluble component, and that the remainder is composed, in about equal proportions, of an insoluble component and a mixture of other soluble components. This view was in opposition to the "two-phase" theory of rubber, according to which rubber hydrocarbon consists of two components, often called sol and gel. Milled rubber, however, was found (191) to consist of a continuous series of soluble components. In another investigation (192), fractional precipitation was used to determine the molecular weight of rubber, as follows: Rubber was combined with sulfur and separated by fractional precipitation into three fractions, which were analyzed for sulfur; as the sulfur contents were found to be in the ratio of 1:2:3, it was assumed that the fractions were the mono-, di-, and tri-sulfides, and from the amount of sulfur present the molecular weight of rubber was calculated.

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[12] Balata is a high polymer which does precipitate in crystalline form.

[13] A good discussion of this work as a whole may be found in Whitby (23).

Kemp and Peters (141) in 1941 attempted to fractionate rubber by cooling a solution in 68:32 benzene–alcohol to 0°C., but found the results disappointing. Rath and Dolmetsch (223) in 1938 suggested that a solution of cellulose in sodium hydroxide could be precipitated fractionally by cooling, as well as by the addition of a precipitant or of acid; it is known from fractional solution studies that the alkali solubility of cellulose is very sensitive to changes of temperature.

(c) Tabular summary of fractional precipitation methods

In order to facilitate a rapid survey of the methods that have been used, the most important facts relating to each are summarized in table 1.

2. Fractional solution

In a fractional solution procedure, the polymer is placed in contact with a solvent–non-solvent mixture, and the system is allowed to come to equilibrium; after the supernatant solution is decanted, the residue is treated with a fresh mixture, richer in solvent than the first, and this process is repeated until the polymer has all dissolved, or until no more will dissolve. In this way the low-molecular fractions are extracted first, the high-molecular ones last.

In this connection, mention should be made of the so-called "solid-phase rule" (14) ("Bodenkörperregel") studied by Ostwald (208, 209, 210) and Neuenstein (200) and noted by Davidson (60). It is based on the observation that the solubility of a polymer, such as cellulose, differs from ordinary solubility in that the amount dissolved depends on the amount of undissolved solid in contact with the solution. This is most readily explained in terms of heterogeneity of the material; in fact, it is rather good proof of the existence of heterogeneity, if indeed any is needed. For, when a certain amount of polymer is in contact with its solution, the solution may be saturated with respect to the high-molecular-weight constituents, but not with respect to the low ones (14); therefore, if the quantity of the solid phase is increased, more of the low-molecular-weight material will go into solution.

The determination of "alkali solubles" (15, 268) is a standard analytical method in cellulose chemistry; in the usual method, three arbitrarily defined fractions, α-, β-, and γ-cellulose, are separated and weighed; these, of course, differ in their average degree of polymerization, and thus the determination shows a good correlation with the mechanical properties that depend on degree of polymerization. For a more exact characterization, Sakurada (229, 230, 231, 232, 234) recommended the determination of the "solubility curve". Among the cellulose solvents, he studied mainly cuprammonium. Brownset and Davidson (45) investigated the solubility in 2.5 *N* sodium hydroxide at −5°C., and Brownset and Clibbens (44) the solubility in Triton B (trimethylbenzylammonium hydroxide) and Triton F (dimethylbenzylammonium hydroxide). The solubility curve is obtained by plotting the amount dissolved against the "solvent power" of the solvent, and the shape of the curve is that of the integral distribution curve (S-shaped). Solvent power depends essentially on the composition of the solution used as solvent (e.g., the concentration of a sodium hydroxide solution, or the copper content of a cuprammonium solution); it can, according to Sakurada (234), be determined by comparing solubility curves of the same sample in a series of liquid mixtures, in which one component is the solvent in question, the other a non-polar indifferent liquid. Taniguchi (288) described a method for determining the "normal" solubility curve by making up a homogeneous mixture of polymer, solvent, and non-solvent (where the solvent has a lower boiling point than the non-solvent), and letting it evaporate very slowly at room temperature; under these conditions precipitation takes place so slowly that entanglement and other intermolecular interaction cannot interfere with it.

Like those involving fractional precipitation, fractional solution procedures can be classified according to whether it is the composition of the extracting mixture or the temperature that is being varied. As there are comparatively few examples of the latter process, the two methods will be discussed together.

(a) Methods of fractional solution

(*1*) *Rubber:* A very important and very thorough study of the fractional solution of rubber was undertaken by Bloomfield and Farmer (39) in 1940. Extreme precautions were taken to avoid degradation: the work was done in a semi-dark room, in an atmosphere of purified nitrogen, and with added antioxidant (β-phenylnaphthylamine); even the acetone extraction of the rubber and the purification of the solvents were carried out under nitrogen. The rubber was extracted continuously, with mixtures of petroleum ether (solvent) and acetone (non-solvent)—25 per cent petroleum ether for the first fraction, 50 per cent for the second, and other suitable mixtures for higher fractions. Three or four extractions were done with separate samples of each mixture, to ensure complete

TABLE 1

Tabular summary of fractional precipitation methods

POLYMER	SOLVENT	PRECIPITANT	CONCENTRATION OF SOLUTION	NUMBER OF FRACTIONS	YEAR OF PUBLICATION	AUTHOR(S) AND REFERENCES
Rubber	Benzene	Benzene–alcohol (1:1)	3%	2	1924	Pummerer and Koch (218)
Rubber	Benzene, hexahydrotoluene, petroleum ether, or ethyl ether	Alcohol or acetone		2	1927	Pummerer and Miedel (219)
Rubber	Varied	Varied	Varied	8	1928	Pummerer and Miedel (220)
Rubber	Benzene or ethyl ether	Ethanol		6	1939	Kovarskaya and Lipatov (147)
Rubber	Chloroform	Methanol			1941	Kemp and Peters (141)
Hydrorubber	Ethyl ether	Ethanol		5	1930	Staudinger and Schaal (280)
Cellulose nitrate	Acetone	Water or acetone–water	5%	3	1920	Duclaux and Wollman (74)
Cellulose nitrate	Acetone	Benzene			1925	Bréguet (41)
Cellulose nitrate	Acetone	Acetone–water (1:1)		2	1928	Kumichel (153)
Cellulose nitrate	Acetone	Water			1929	Duclaux and Nodzu (73)
Cellulose nitrate	Acetone	Water–acetone (1:4)	16%	4	1930	Beck, Clément, and Rivière (35)
Cellulose nitrate	Acetone–water	Vacuum distillation	5%	11	1930	Beck, Clément, and Rivière (35)
Cellulose nitrate	Acetone	Water			1933	Duclaux and Barbière (72)
Cellulose nitrate	Acetone	Water		9	1933	Medvedev (182); Medvedev and Denisov (183)
Cellulose nitrate	Acetone, ethyl acetate, or benzene	Water			1934, 1935	Glikman (Glückmann) (107–109, 111 112)
Cellulose nitrate	Acetone–water	Vacuum or ordinary distillation			1935	Glikman (111)
Cellulose nitrate	Acetone	Water		3	1935	Rogovin and Glazman (225)
Cellulose nitrate	Acetone	Water			1936	Schulz (243)
Cellulose nitrate	Acetone	Heptane		17	1938	Spurlin (264)
Cellulose nitrate	Acetone	Water or ethanol			1938	Rath and Dolmetsch (223)
Cellulose nitrate	Acetone	Water		4–7	1939	Staudinger and Jurisch (278)
Cellulose nitrate	Acetone	Water	0.5%		1940	Jurisch (138)
Cellulose nitrate					1941–1942	Schulz *et al.* (252, 254)
Cellulose acetate	Acetone	Water			1923	Mardles (172)

Cellulose acetate	Acetone	Acetone-water (1:1)	3%		1928	Caille (46)
Cellulose acetate	Acetone	Water-acetone (3:1)	10%		1929	McNally and Godbout (171)
Cellulose acetate	Acetone	Water		3	1930	Rocha (224)
Cellulose acetate	Acetone	Water		3	1930, 1932	Ohl (205, 206)
Cellulose acetate	Acetone	Water			1931	Iwasaki (130)
Cellulose acetate	Acetone	Water			1931	Caille (47)
Cellulose acetate	Methyl glycol or acetone	Water or petroleum ether			1932	Herzog and Deripasko (119)
Cellulose acetate	Acetone	Water			1934	Clément and Rivière (53)
Cellulose acetate	Acetone	Water			1934	Obogi and Broda (203)
Cellulose acetate	Acetone	Water			1934	Herz (117)
Cellulose acetate	Chloroform	Methanol			1934	Elöd and Schmid-Bielenberg (77)
Cellulose acetate	Chloroform	Methanol			1934	Hess and Ulmann (120)
Cellulose acetate	Acetone	Water	2.5%		1935	Ulmann (293)
Cellulose acetate	Acetic acid-acetone (1:1)	Water		4	1937, 1939	Lachs *et al.* (155-159)
Cellulose acetate	Chloroform	Methanol			1937, 1939	Lachs *et al.* (155-159)
Cellulose acetate	Acetone	Benzene			1938	Levi, Villotta, and Monticelli (164)
Cellulose acetate	Acetone	Ethyl ether			1939	Danilov, Gol'dfarb, and Zaitseva (59)
Cellulose acetate	Acetic acid	Water			1939	Bezzi and Croatta (37)
Cellulose acetate	Acetone	Water			1940	Mark and Simha (180)
Cellulose acetate	Acetone	Ethanol	2.5%	15	1942	Sookne, Rutherford, Mark, and Harris (263)
Ethyl cellulose	Glacial acetic acid	Water			1933	Okamura (207)
Benzyl cellulose	Alcohol-benzene	Alcohol			1936, 1937	Glikman (Glückmann) (110, 113)
Methyl cellulose	Water	Sodium sulfate	2.5%	4	1938	Signer and Liechti (259)
Ethyl cellulose	Dioxane	Water		3	1938	Staudinger and Reinecke (279)
Ethyl cellulose	Alcohol	Gasoline	4%		1939	Ushakov *et al.* (294)
Cellulose xanthogenate	Aqueous pyridine	Methanol or ether	Very dilute		1934	Fink, Stahn, and Matthes (85)
Cellulose	Sodium hydroxide	Sodium sulfate	0.1%		1939	Tydén (291)
Cellulose	0.5 *M* cupriethylenediamine	8 *N* sulfuric acid	1%	8	1942	Strauss and Levy (284)
Cellulose	Sodium hydroxide	Water-acetone			1943	Coppick, Battista, and Lytton (55)

TABLE 1—*Continued*

POLYMER	SOLVENT	PRECIPITANT	CONCENTRATION OF SOLUTION	NUMBER OF FRACTIONS	YEAR OF PUBLICATION	AUTHOR(S) AND REFERENCES
Gelatin	Water	Alcohol		2	1926	Northrop and Kunitz (202)
Gelatin	Water	Ammonium sulfate		2	1927	Nagorny (199)
Glycogen	Formamide	Methanol			1937	Staudinger and Husemann (277)
Glycogen (degraded)	0.1 *N* calcium chloride	Methanol		3	1941	Husemann (129)
Dextrin	Water	Methanol			1942	Levine, Foster, and Hixon (165)
Nitrated wood	Acetone	Alcohol-water		8	1943	Coppick and Jahn (56)
Polyvinyl acetate	Benzene	Petroleum ether	40%	3	1927	Staudinger *et al.* (275)
Polystyrene (hemicolloidal)	Acetone	Acetone	37%	5	1929	Staudinger *et al.* (273)
Polyethylene oxide	Benzene	Ethyl ether		3	1929	Staudinger and Schweitzer (281)
Polyindene	Benzene	Ethanol		7	1928	Whitby and Katz (300)
Polycinnamalfluorene	Benzene	Ethanol		5	1928	Whitby and Katz (300)
Polycinnamalindene	Benzene	Ethanol		4	1928	Whitby and Katz (300)
Polystyrene	Benzene	Ethanol	1.5%	3	1930	Whitby (297)
Polyindene	Chloroform	Ethanol	40%	3	1930	Whitby and Katz (299)
Polystyrene	Benzene	Ethanol		6	1932	Whitby (298)
Polystyrene	Benzene	Acetone		4	1932	Staudinger (21)
Polystyrene	Benzene	Methanol-acetone			1934	Daneš (58)
Polystyrene	Methyl ethyl ketone	Methanol		7	1936	Schulz and Husemann (251)
Polystyrene	Chloroform, benzene, tetralin, carbon disulfide, dioxane, or pyridine	Methanol			1936	Dobry and Schwob (67)
Sodium butadiene polymer	Benzene	Methanol, ethanol, propanol, phenol, or acetone	Varied		1936	Komarov and Selivanova (146)
Vinyl ester	Acetone	Acetone-water			1936	Douglas and Stoops (71)
Sodium bivinyl polymer	Benzene	Ethanol	1%	4	1938	Zhukov and Komarov (305)
Polymethyl methacrylate	Benzene	Cyclohexane			1941	Schulz and Dinglinger (250)
Polyvinyl acetate	Acetone	Methanol-water (1:1)			1941	Blease and Tuckett (38)

Polyvinyl chloride......	Mesityl oxide or cyclohexanone	Methanol (acetone as diluent)	0.5–1%		1941	Fuoss (95)
Polyisobutylene...........	Benzene	Acetone	5%	5	1941	Kunc and Miller (310)
Polyisobutylene	Carbon disulfide	Ethyl ether	10%	8	1941	Kunc and Miller (310)
Polyisobutylene......	Benzene or toluene	Acetone or methanol			1942	Staudinger *et al.* (270)
Polymethacrylonitrile ..	Acetone	Methanol	1%		1942	Kern and Fernow (145)
Polyvinyl chloride	Acetone	Methanol			1943	Fuoss and Mead (96)
Polyisobutylene ..	Benzene	Acetone	1%		1943	Flory (90)
Polystyrene ..	Methyl ethyl ketone	Methanol	2%	20	1943	Alfrey, Bartovics, and Mark (27)
Buna S. .	Benzene	Methanol	2%	2	1944	Kemp and Straitiff (144)
Cellulose acetate .	Benzene–methanol or benzene–ethanol	Cooling	10%		1929	British Celanese Ltd. (308)
Balata	Benzene, toluene, or xylene	Cooling	3–4%	5	1930	Staudinger and Bondy (271)
Cellulose acetate....... . .	Benzene–ethanol or benzene–methanol	Cooling	5–15%	2	1934	Scheidegger (311)
Rubber.....	Alcohol–benzene	Cooling		7	1931–1942	Midgley *et al.* (186–193)
Rubber. . . .	Alcohol–benzene	Cooling	3%	Unsuccessful	1941	Kemp and Peters (141)
Cellulose	Sodium hydroxide	Cooling			1938	Rath and Dolmetsch (223)

extraction of that fraction. The extractions were carried out under static conditions, except for slow rotation on rollers about a horizontal axis for 2-hr. periods. The fractions were isolated by evaporation under reduced pressure in a current of nitrogen. Four fractions were obtained. Their physical properties were measured by Gee and Treloar (103), and relationships between molecular weight and physical properties established.

A similar method was used by Kemp and Peters (141) in 1941, with acetone–hexane mixtures as solvents for the extraction. Light was excluded, and the work was done under nitrogen.

(2) Cellulose and its derivatives: Uchida (292) in 1930 determined the solubilities of nitrocellulose in a variety of ethyl ether–ethanol mixtures at various temperatures, and characterized the soluble and insoluble fractions by their nitrogen contents.

The first thorough study in the field is due to Craik and Miles (57), who in 1931 fractionally extracted nitrocellulose with acetone–water solutions at controlled temperatures. The advantage claimed for this method as compared with Duclaux's precipitation method is that any number of fractions can easily be obtained. Two variations of the method were used: one in which the residue insoluble in one solution was subsequently treated with one richer in solvent; and another "analytical" one, in which a fresh sample was used every time, and treated with the various solutions. The viscosities of the fractions were found to differ.

In 1933, Berl and Hefter (36) fractionated nitrocellulose by extraction with ethyl ether–ethanol solutions; the nitrogen contents of the fractions usually differed. In the same year, Yamamoto (304) fractionally extracted nitrocellulose with acetone–water solutions; in this case also, separation according to the degree of nitration resulted.

In 1934, Clément and Rivière (53) studied the fractional solution of cellulose acetate, using aqueous methanol or aqueous ethanol. Again, the fractions differed chemically as well as in physical properties. In the same year, Taniguchi and Sakurada (289) applied a similar procedure to cellulose dextrin acetate, and to triacetylcellulose. Acetone–benzene solutions were used in each case; the cellulose dextrin acetate yielded five fractions, the triacetylcellulose four.

In 1934 also, Correns (309) invented a process in which cellulose acetate was fractionally dissolved in various mixtures of acetone and ethanol; the insoluble fraction showed superior properties for the production of films and filaments, while the soluble part was suitable for lacquers.

In the same year, Fink, Stahn, and Matthes (85) effected a fractionation of cellulose xanthogenate (viscose) by extraction with aqueous pyridine or dioxane. The two fractions obtained differed both in chain length and in chemical composition.

Davidson in 1934 (60) and 1936 (61) studied the solution of modified cellulose (oxy- and hydro-celluloses) in the hydroxides of sodium, lithium, potassium, and tetramethylammonium. A fractional extraction of hydrocellulose with sodium hydroxide was effected by varying the concentration (from 2.25 *N* to

2.5 *N*) and the temperature (from 0°C. to −5°C.). The dissolving power of lithium hydroxide and tetramethylammonium hydroxide proved to be similar, but that of potassium hydroxide was less, and not as much affected by temperature.

Abel and Hess (24) in 1935 observed that the extract of trimethylcellulose with hot benzene yields, on cooling, one fraction that is soluble in cold benzene, and another that is insoluble. By repeating the procedure, a reversibly soluble fraction was finally obtained. These effects, which the authors call "false solubility", are readily explained on the basis of heterogeneity—the reversibly soluble fraction has become reasonably homogeneous because of repeated fractionation. The action of other solvents was described.

In 1935, Staud and Yackel (312) described a process for fractionating cellulose acetate on a commercial scale by stirring it with a solvent mixture consisting of acetone and water, or acetic acid and water. They claimed that the residue (which showed a higher viscosity than the soluble fraction, but the same acetyl content) gave more flexible and more water-resistant films than the original material.

Mark and Saito (179) in 1936, in reviewing various possible fractionation procedures for cellulose acetate, mentioned fractional solution with benzene–methyl acetate mixtures. The fractions were said to differ in viscosity, but not in acetyl content. In the same year Rogovin and Glazman (226) fractionated cellulose acetate by solution in acetone–water mixtures and found that separation with respect to chemical nature could be effected. Neumann, Obogi, and Rogovin (201) in 1936 treated cellulose from three sources (cotton linters, sulfite pulp, and viscose rayon) by two fractional solution methods: (*1*) using sodium hydroxide of fixed concentration and changing the temperature; (*2*) using cuprammonium solution of varying copper content. In (*1*), the sodium hydroxide concentration was 12 per cent, the time of extraction 30 min., and the temperature 15°C., 0°C., −5°C., and −12°C.

O'Dwyer (204) in 1937 separated oak hemicellulose into two fractions by digesting the sample with the enzyme takadiastase and extracting with water, or, as in one case, by extracting with water without the prior use of an enzyme.

Kumichel (154) in 1938 described the fractional solution of cellulose in cuprammonium solutions of gradually increasing copper content. Rath and Dolmetsch (223) in 1938 used fractional solution of nitrocellulose in acetone–water solutions. Dolmetsch and Reinecke (68, 69) in 1939 extracted cellulose with 10 per cent sodium hydroxide (making temperature the variable), and nitrocellulose with various mixtures of acetic acid and ethanol, or acetone and ethanol. In 1939, Schieber (238, 239, 240, 241) discussed the fractionation of cellulose, and came to the conclusion that fractional solution in sodium hydroxide is unsatisfactory, because the solubility of the high fractions is too low and there is a danger of degradation. He nitrated the cellulose carefully, using a mixture of phosphoric acid and fuming nitric acid at 18°C., and fractionated the nitrate by solution in ethanol–ethyl acetate or ethanol–acetic acid mixtures. Böhringer and Seyfert (40) in 1939 studied the changes in molecular-weight distribution that take place on washing and bleaching textiles, by means of fractional solution of the nitrate. Eisenhut (75) in the same year recommended fractional washing with sodium hydroxide, as a method for characterizing staple fiber. Morozov (196), in 1939, fractionated cotton cellulose with a mixture containing 1.35 per cent copper, 15.5 per cent ammonia, and 0.02 per cent sucrose, and other mixtures prepared from the first one by stepwise dilution with water.

Staudinger and Eder (274) in 1941 fractionated highly degraded cellulose triacetate by solution in chloroform.

In 1942, Ekenstam (76) used phosphoric acid of varying concentration in the range of 73–83 per cent for the fractional solution of the cellulose in rayon pulp and in finished rayon.

In 1943, Atchison (27a) described in some detail the fractionation of several cellulose nitrates. As extracting media, he used solutions of ethyl acetate and absolute ethyl alcohol.

(3) *Other natural products:* In 1935, Liepatoff and Putilowa (166) applied the method to gelatin, using water at various temperatures, and obtained four fractions. Lampitt, Fuller, and Goldenberg (161) in 1941 treated starch in a similar way and obtained a water-insoluble fraction (α-amylose), a fraction soluble in hot water (β-amylose), and one soluble in cold water ("soluble starch").[13a]

(4) *Synthetic products:* Staudinger, Frey, and Starck (275) reported two methods for fractionating polyvinyl acetate in 1927: the first, by precipitation, has already been described; in the second one fraction was obtained by extracting with butanol, another by dissolving the residue in benzene and precipitating with butanol, and a third from the resulting supernatant liquid. Staudinger (20) described a fractional solution method for hemicolloidal polystyrenes, in which, instead of using binary mixtures of varying composition, he used different single solvents in succession for the extraction. Methanol was used to dissolve out the lowest members (degree of polymerization 1–10), hot butanol the next fraction (10–30), and acetone the higher members (30–60); fractional precipitation with acetone or methanol was used for the highest members.

In 1936, Douglas and Stoops (71) reported an analytical precipitation procedure for vinyl esters; this has been described above. In order to determine the width of the bands in this procedure, they fractionated two of the resins completely by a fractional extraction process, obtaining twenty-five fractions from each. A similar purpose was served by the fractionation of coumarone–indene varnish resin reported by Adams and Powers (25) in 1943; these authors wished to correlate their precipitation titration studies with an actual distribution curve, and for that purpose fractionated the above-mentioned resin by fractional solution, obtaining seven fractions.

Rogovin and Tsaplina (227) in 1941 demonstrated the polydispersity of samples of polyvinyl chloride by fractional solution in acetone at room temperature and at 40–45°C.

[13a] A recent review, by T. J. Schoch, of methods in use for the separation of starch into the usual two fractions may be found in *Advances in Carbohydrate Chemistry*, Vol. I, W. W. Pigman and W. L. Wolfrom (*Editors*), pp. 247–77. Academic Press, Inc., New York (1945).

Sebrell (256) in 1943, in the course of a comparison of the properties of natural rubber with those of several synthetic rubbers, carried out a fractionation of Buna S by extraction with petroleum ether–benzene solutions, and alcohol–petroleum ether solutions for the lowest members. It was found that fractionation is less efficient in the high than in the low molecular-weight range. A more rapid (analytical) method was also tried, in which separate portions of the original sample were extracted with the various mixtures.

Kemp and Straitiff (144) in 1944 described a method for extracting the low polymer from Buna S by using methanol–benzene solutions, of a concentration in the neighborhood of 20 per cent by volume of methanol. The extracted fraction constituted 42 per cent of the original by weight.

(b) Tabular summary of fractional solution methods

The methods described above are summarized, for more convenient reference, in table 2.

3. Comparison of fractional precipitation and fractional solution methods

There have been many objections raised against fractional precipitation methods. Craik and Miles (57) criticized Duclaux's (74) method on the grounds that (*1*) 5 per cent of the original material is lost in the precipitations, (*2*) when water is added drop by drop, three layers are sometimes formed, which can be separated only with difficulty, (*3*) there is little choice as to the size and number of fractions, for the first one is always large (50–75 per cent of the total). They claimed that with solution methods any number and size of fractions can be obtained, and that there are no losses in the process. Rogovin and Glazman (226) also pointed out the disadvantages of Rocha's (224) method, claiming (*1*) that overlapping of fractions occurs because the longer molecules pull the shorter ones down into the precipitate while the shorter keep the longer ones in solution, by entanglement and other forms of interaction, (*2*) that the reproducibility of the results is not good, (*3*) that a limited number of fractions only can be obtained in one run, so that refractionation is necessary, and (*4*) that fractionation is effected only with respect to molecular size, not with respect to the degree of chemical substitution. Dolmetsch and Reinecke (68) claimed that precipitation methods suffer from (*1*) an overlapping of fractions as a result of entanglements, (*2*) lack of reproducibility, and (*3*) the difficulty of making a clean separation of the two phases. Sakurada and Taniguchi (235) also drew attention to several disadvantages of the method: (*1*) the initial complete solution that is necessary can often be effected only by means that cause partial breakdown; (*2*) results are difficult to reproduce for, since equilibrium is attained so slowly, the amount of precipitate depends on the length of the interval between the addition of precipitant and separation; and (*3*) a substance that, when added in certain proportions, can decrease the dissolving power of a solvent—and thereby act as a precipitant—may in other proportions actually increase it. Bloomfield and Farmer (39) adopted the fractional solution procedure (at Gee's suggestion)

TABLE 2

Tabular summary of fractional solution methods

POLYMER	EXTRACTING MIXTURE	VARIABLE	NUMBER OF FRACTIONS	YEAR OF PUBLICATION	AUTHOR(S) AND REFERENCES
Rubber	Petroleum ether–acetone	Composition	4	1940	Bloomfield and Farmer (39)
Rubber	Hexane–acetone	Composition		1941	Kemp and Peters (141)
Cellulose nitrate	Ethyl ether–ethanol	Composition or temperature	2	1930	Uchida (292)
Cellulose nitrate	Acetone–water	Composition		1931	Craik and Miles (57)
Cellulose nitrate	Ethyl ether–ethanol	Composition		1933	Berl and Hefter (36)
Cellulose nitrate	Acetone–water	Composition		1933	Yamamoto (304)
Cellulose acetate	Water–methanol (or ethanol)	Composition		1934	Clément and Rivière (53)
Cellulose acetate	Acetone–ethanol	Composition	2	1934	Correns (309)
Cellulose dextrin acetate	Acetone–benzene	Composition	5	1934	Taniguchi and Sakurada (289)
Cellulose triacetate	Acetone–benzene	Composition	4	1934	Taniguchi and Sakurada (289)
Cellulose xanthogenate	Pyridine–water or dioxane–water		2	1934	Fink, Stahn, and Matthes (85)
Oxycellulose or hydrocellulose	Hydroxides of sodium, lithium, potassium, or tetramethylammonium	Composition or temperature		1934, 1936	Davidson (60, 61)
Trimethylcellulose	Benzene	Temperature		1935	Abel and Hess (24)
Cellulose acetate	Acetone–water or acetic acid–water		2	1935	Staud and Yackel (312)
Cellulose acetate	Benzene–methyl acetate	Composition		1936	Mark and Saito (179)
Cellulose acetate	Acetone–water	Composition		1936	Rogovin and Glazman (226)
Cellulose	Sodium hydroxide (12%)	Temperature		1936	Neumann, Obogi, and Rogovin (201)
Cellulose	Cuprammonium	Copper content		1936	Neumann, Obogi, and Rogovin (201)
Oak hemicellulose	Enzyme digestion and water		2	1937	O'Dwyer (204)
Cellulose	Cuprammonium	Copper content		1938	Kumichel (154)
Cellulose nitrate	Acetone–water	Composition		1938	Rath and Dolmetsch (223)
Cellulose	Sodium hydroxide (10%)	Temperature		1939	Dolmetsch and Reinecke (68, 69)
Cellulose nitrate	Acetic acid–ethanol or acetone–ethanol	Composition		1939	Dolmetsch and Reinecke (68, 69)
Cellulose	Sodium hydroxide	Temperature		1939	Schieber (238–241)

Cellulose nitrate	Ethanol-ethyl acetate or ethanol-acetic acid	Composition		1939	Schieber (238-241)
Cellulose nitrate	?			1939	Böhringer and Seyfert (40)
Cellulose	Sodium hydroxide	?		1939	Eisenhut (75)
Cellulose	Cuprammonium	Concentration		1939	Morozov (196)
Degraded cellulose triacetate	Chloroform			1941	Staudinger and Eder (274)
Cellulose	Phosphoric acid (73-83%)	Concentration		1942	Ekenstam (76)
Cellulose nitrate	Ethanol-ethyl acetate	Composition		1943	Atchison (27a)
Gelatin	Water	Temperature	4	1935	Liepatoff and Putilowa (166)
Starch	Water	Temperature	3	1941	Lampitt, Fuller, and Goldenberg (161)
Polyvinyl acetate	Butanol-benzene	Composition		1927	Staudinger, Frey, and Starck (275)
Hemicolloidal polystyrene	Methanol-butanol-acetone	Nature of solvent		1932	Staudinger (20)
Polyvinyl esters	?		25	1936	Douglas and Stoops (71)
Polyvinyl chloride	Acetone	Temperature		1941	Rogovin and Tsaplina (227)
Coumarone-indene resin	?		7	1943	Adams and Powers (25)
Buna S	Petroleum ether-benzene or alcohol-petroleum ether	Composition		1943	Sebrell (256)
Buna S	Methanol-benzene		2	1944	Kemp and Straitiff (144)

mainly because of the danger of entangled clusters of molecules precipitating "en bloc" in a fractional precipitation method.

Most of the objections to fractional precipitation disappear when the solution is made sufficiently dilute. Precipitation "en bloc" occurs only when the solution is concentrated enough to allow interaction between the molecules; moreover, there is no reason why chain entanglements in the solid sample should not cause a similar difficulty in the solution process. It is true, of course, that solution occurs much more slowly than precipitation, as ordinarily carried out, and hence equilibrium conditions are more likely to be maintained. However, precipitation by cooling can be made to occur as slowly as desired; and even if precipitation be carried out by the addition of precipitant, the technique of heating the mixture above the critical temperature and allowing the final precipitation to occur by slow cooling can always be used. Moreover, if the solution is dilute enough, a greater number of small fractions can be obtained than in a more concentrated one, as may be seen by a consideration of the phase diagram. Diluting the precipitant with the solvent, or with a third liquid, improves the control of precipitation conditions, as does working at a higher temperature, where the solubility is greater. As for the necessity for refractionation, such treatment is desirable (99) in any case, if uniform fractions are to be obtained. Indeed, Spurlin (264) rejected fractional solution in favor of precipitation because the former method does not so readily permit refractionation.

Mark (176) suggested that it would be profitable to compare results obtained by the two methods when used on the same material. He found that, in the case of cellulose nitrate precipitated with heptane from butyl acetate or acetone solution and extracted with alcohol–ethyl acetate mixtures of varying compositions at constant temperature, the results of the two methods were in good agreement.

Kemp and Peters (141) made a comparison of several procedures as applied to rubber: fractional diffusion into a single solvent (to be discussed in the next section), fractional solution by a method similar to that of Bloomfield and Farmer, combined diffusion and precipitation, and fractional cooling; they decided in favor of the combined diffusion and precipitation process.

Jurisch (138) prefers precipitation to solution methods. He considers the latter to have the following disadvantages: (*1*) there is considerable overlapping of the molecular-weight ranges of the fractions (as he showed by comparison with fractional precipitation results obtained for the same sample); (*2*) the swelling of the undissolved residue is so great that the solvent power of extracting mixtures cannot be increased beyond a certain value, without making the phases very difficult to separate; (*3*) insoluble impurities accumulate in the residue, whereas in fractional precipitation they can be removed by filtering before the precipitant is added.

For the fractionation of cellulose, however, solution methods are usually preferable to precipitation. As Neumann, Obogi, and Rogovin (201) pointed out, it is extremely difficult to effect complete solution of a cellulose sample in any solvent, without risking the danger of breakdown by the drastic treatment necessary. In spite of this difficulty, however, Coppick, Battista, and Lytton (55) succeeded in dissolving cellulose completely in sodium hydroxide, and were thus able to fractionate it by precipitation. Another solvent, in which complete solution is claimed to take place easily without degradation, is cupriethylenediamine, as suggested by Strauss and Levy (284).

Some polymers are heterogeneous in more than one respect. The molecules of cellulose nitrate, for example, differ both in chain length and in degree of nitration. In such instances it may be desirable sometimes to prepare fractions of relatively uniform chain length, at other times fractions of relatively uniform composition. No method has been reported that effects a separation solely on the basis of composition, but many methods yield fractions that differ from each other in both respects. (For examples, see previous sections and references 36 and 179.) If from a fractionation study conclusions are to be drawn as to relationships between chain length and physical properties, it should always be definitely established that the fractions are identical in chemical composition.[14]

4. *Distribution between two immiscible solvents*

In precipitation and solution methods, the solvent and non-solvent are completely miscible; only the presence of polymer (in amounts above the critical value) causes a separation into two phases. It is also possible, however, to use a solvent system which is heterogeneous even in the absence of polymer; as Brønsted (42) and Schulz and Nordt (255) have shown, the distribution of polymer molecules in such a system depends on molecular weight. A fractionation can, therefore, be accomplished by varying the composition of one of the phases.

Such a method was applied in 1940 by Schulz and Nordt (255) to polyethylene oxide (which they found could not be fractionated by precipitation, because the crystalline nature of the precipitate made it difficult to maintain equilibrium). In the solvent system one phase was water, and the other a solution of chloroform and benzene; the percentage of benzene was decreased stepwise in the separation of successive fractions. The volume of the water layer was kept large compared to that of the other, for theoretical considerations showed that this improved the efficiency of separation. In order to ensure equilibrium and yet prevent emulsification, the two phases were stirred separately and in opposite directions.

A similar method was applied in 1941 by Lovell and Hibbert (169) to lignin. They used the solvent system methanol–water–chloroform–carbon tetrachloride, effecting separation by varying the concentration of the chloroform. Fractions differed both in viscosity and in methoxyl content.

Although this method has as yet been applied only in these two instances, it could be used with any high polymer, provided that a suitable solvent system could be found. Schulz and Nordt (255), however, express the opinion that fractional precipitation is more efficient and should be used in preference whenever applicable.

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[14] It is important to note that such considerations apply especially to synthetic copolymers, for in such substances compositional heterogeneity is the rule. For example, Buna S molecules of the same weight may differ widely in styrene content.

B. RATE-OF-SOLUTION (DIFFUSION) METHODS

Although the methods to be described in this section are sometimes classed with fractional solution methods, they should be treated separately, as they are based on a different principle. The separation according to molecular size does not, as in the previous section, depend on the difference in the solubility of the larger and the smaller molecules, but on the difference in their rate of solution or diffusion. Whereas in solubility methods equilibrium conditions prevail (or should prevail), in diffusion methods fractions are separated as they are still diffusing, before equilibrium is established. The method involves placing the polymer in contact with a solvent, removing the supernatant solution after a definite time interval, replacing it with fresh solvent, and repeating the procedure until the desired number of fractions has been obtained. As would be expected, the smaller molecules concentrate in the first fractions and the larger ones in the last, for the smaller molecules diffuse more rapidly and are, therefore, first extracted.

Although fractional solution and diffusion differ in principle, it is often difficult to classify a particular method, because of an uncertainty as to whether or not equilibrium conditions existed. In this review we have classified as diffusion methods those in which a single solvent is used, at a single temperature, in successive extractions; and as fractional solution methods those in which either the composition of a mixed solvent, or the temperature at which it is used, is varied in successive extractions. It is freely admitted that this classification is somewhat arbitrary, as it is possible to separate two fractions (but not more than two) by extraction with a single solvent at a single temperature, when equilibrium conditions are maintained.

(a) Applications of the diffusion methods

(1) Rubber: Most of the diffusion experiments have been done with natural rubber, and are closely associated with early theories about the "two-phase" nature of rubber.

As early as 1887, Engler and Herbst (79) knew that rubber is only partly soluble in solvents such as ether, chloroform, benzine, benzene, and carbon disulfide; they described the properties of the two fractions obtainable, and concluded that "in rubber two isomers are combined". Gladstone and Hibbert in 1888 (106) confirmed these observations. Weber (295, 296) in 1900 described an extraction with chloroform, and concluded that the fractions are not chemically identical, as the insoluble part contained combined oxygen. In 1912, Beadle and Stevens (34) used benzene for the separation, and likewise emphasized the lack of purity of the insoluble fraction, focusing attention, however, on the nitrogen rather than the oxygen content. Caspari (51) in 1913 recommended petroleum ether as the solvent, because it gives a more complete separation and produces less swelling of the insoluble part, thus giving a more distinct boundary between the phases. The terms "soluble" and "pectous" (insoluble) rubber were applied to the two fractions. Two extraction methods were described: one continuous, by which quantitative separation was claimed to have been effected after 10 hr.; the other, static. These experiments were criticized in 1919 by Stevens (282), who pointed out that the amount dissolved depends on many variables besides the nature and source of the rubber,—namely, the nature of the solvent, the time of extraction, the temperature, and the age of the specimen. In 1925 Feuchter (84) used ethyl ether and petroleum ether as the solvent; he called the two fractions diffusion (or D) rubber, and gel skeleton.

TABLE 3

Tabular summary of diffusion methods

POLYMER	SOLVENT	AUTHOR(S) AND REFERENCES
Rubber	Petroleum ether	Caspari (51), Feuchter (84), Kemp and Peters (139), Gee (97)
	Ethyl ether	Engler and Herbst (79), Feuchter (84), Pummerer *et al.* (214–217, 220, 222), Smith *et al.* (260–262), Midgley and Henne (188)
	Chloroform	Engler and Herbst (79), Weber (295, 296)
	Benzene	Engler and Herbst (79), Beadle and Stevens (34)
	Carbon disulfide	Engler and Herbst (79)
	Hexane	Kemp and Peters (139, 141)
Nitrocellulose in acetone solution	Acetone	Krüger (152)
Nitrocellulose	Ethanol	Duclaux and Nodzu (73)
Polyanethole	Ethyl ether	Staudinger *et al.* (272)
Polyindene	Ethyl ether or petroleum ether	Staudinger *et al.* (269)
Polyvinyl acetate	Acetone	Whitby, McNally, and Gallay (301)
Polystyrene	Ethyl ether, acetone, or diethyl oxalate	Whitby (297)
Sodium bivinyl polymer	Petroleum ether, benzene, or chloroform	Zhukov *et al.* (306)

In the same year, the two-phase theory received further support from a study of the structure of latex particles, by Freundlich and Hauser (93); they found, by using a micromanipulator, that Hevea latex particles consist of a fluid interior (identified with the soluble fraction) surrounded by a solid shell (the gel skeleton) (see also Hauser (3)).

The work of Pummerer (214, 215, 216, 217, 220, 222), on the other hand, threw doubt on the theory. In 1926 he observed (214) that, although the rate of solution of rubber becomes very slow after about 3 days in contact with ethyl ether, diffusion does not entirely stop; and also, that milling increases the proportion of the soluble component. It was in this paper that the terms "sol" and "gel" rubber were introduced. In 1928, Pummerer *et al.* (217) described a continuous extraction apparatus for the fractionation of rubber; a fraction was defined as the portion of rubber extracted in 24 hr. In another paper, Pummerer and Miedel (220) compared the extraction process with other purification methods (including fractional precipitation) with respect to the efficiency of purification. Later Pummerer and Pahl (222) described a static extraction with ethyl ether, in which six successive samples of ether were allowed to remain for 3 days in contact with the rubber sample (air and light carefully excluded) and then poured off.

In 1928, Bary and Hauser (32, 33) recommended the terms α- and β-rubber instead of sol and gel. They contended that the possibility of a reversible transformation of α- into β-rubber shows that they form a one-phase system (a jelly), not a two-phase system (a gel); that there may be two components, but not two phases, in the rubber hydrocarbon. An attempt was made to explain the elastic properties of rubber on this basis.

Whitby (297) in 1930 definitely proved that diffusion of rubber into organic solvents never comes to an abrupt end, but rather slows down gradually; he found that after four years one sample was completely dissolved, except for the protein. Even if the point where diffusion becomes very slow is taken as the "end point", the sol–gel ratio still depends on the nature of the solvent. He therefore concluded that instead of a pair there is a continuous series of components, as in synthetic polymers such as polystyrene or polyvinyl acetate. He reaffirmed this in 1932 (298).

In 1933 and 1934, Smith *et al.* (260, 261, 262) prepared pure rubber hydrocarbon, crystallized it, and then separated it into sol and gel by extraction with ethyl ether; they also succeeded in crystallizing the sol and gel fractions, and examined their properties.

Staudinger (22) fractionated rubber by diffusion, and found that the molecular weights of the four fractions differed only slightly.

Midgley and his collaborators (187, 188) again pointed out the fallacy of the two-phase theory. The early workers took it for granted that sol and gel could be separated by extraction with ether, just as sugar and sand would be separated by extraction with water; actually, however, sol and gel are mutually soluble. On the addition of ether, two phases are formed, but these do not correspond to sol and gel; the solution phase consists of the sol fraction and ether, while the insoluble phase contains some sol in addition to gel and ether. There is, therefore, no absolute method for determining sol–gel ratios.

More recently, Kemp and Peters (139) have studied the fractional diffusion process, as applied to rubber. In 1939 they described the method and the apparatus. The solvent was petroleum ether or hexane, the extraction period 72 hr., and the work was carried out under an atmosphere of nitrogen and at a constant temperature. (Petroleum ether was found superior to ethyl ether, as the latter is apt to contain peroxides and therefore cause oxidative breakdown; hexane is even better than petroleum ether. Hexane is also preferable to benzene or tetralin.) In 1941 (141), the same method (with hexane as solvent) was compared with other fractionation procedures; twelve fractions were then obtained. In a combined diffusion and precipitation method, already described, chloroform was used as the solvent.

Gee (97) in 1940 used petroleum ether in the preparation of sol rubber for osmotic-pressure determinations.

The modern ideas about the structure of the rubber hydrocarbon, as far as the sol and gel components are concerned, can be summarized as follows: (*1*) there is no single sol component, but a continuous series of components, differing in the degree of polymerization only, and thus constituting a homologous polymeric series; (*2*) the gel component differs from the sol components in that it is cross-linked (13);[15] (*3*) the sol and gel form a one-phase system; (*4*) the sol–gel ratio can be changed by various treatments, e.g., milling (and therefore reversible sol–gel transformations are possible); (*5*) it is not definitely known what the native state of rubber is, before any treatment is applied. Staudinger (19) suggested that rubber and cellulose may be monodispersed in the native state, and be broken down and made heterogeneous by purification and other treatments. Treatment could cause both depolymerization of the chains, or their cross-linking (e.g., by the action of oxygen or light).

An interesting comparison between an extraction and a precipitation method of fractionation was made by Midgley and Henne (188). They found that sol rubber prepared by a single diffusion into ethyl ether can be separated into two fractions by precipitation from benzene–alcohol by cooling, but the sol prepared by precipitation diffuses completely in ether; this proves the superiority of the precipitation method. Gee (99), in discussing various fractionation procedures, expressed doubt as to whether fractional extraction by a single solvent can ever be made quantitatively reproducible.

(*2*) *Cellulose and its derivatives:* Applications of the fractional diffusion method to cellulose and its esters and ethers are rare.

Krüger (152) in 1928 used a method in which diffusion took place not from the solid phase, but from a solution; he let 20 cc. of a solution of nitrocellulose in acetone, methanol, amyl acetate, and other solvents diffuse against 60 cc. of the pure solvent; after a definite time, four layers could be separated, which differed both in molecular weight and in degree of nitration. Duclaux and Nodzu (73) in 1929 mentioned that nitrocellulose can be fractionated by solution in ethanol.

McNally and Godbout (171) in 1929 used a method which bears the same relationship to diffusion into a single solvent as fractional precipitation does to fractional solution; it, too, depends on the rate of a process rather than on the equilibrium state, but it involves precipitation rather than solution. They added suitable amounts of water to an acetone solution of cellulose acetate, and collected the precipitate formed after various lengths of time.

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[15] It might be better to say that the essential difference between sol and gel is one of molecular size. In the preparation of most synthetic polymers branching and cross-linking are probably occurring at all stages of the polymerization. The resulting molecules belong to the gel component when they have reached such a size that they are insoluble (under the conditions of the experiment) in the solvent in question.

(*3*) *Synthetic products:* Whitby *et al.* (301) fractionated polyvinyl acetate in 1928 by diffusion into acetone, and obtained four fractions. In 1930, they (297) extracted polystyrene with each of the solvents ether, acetone, and diethyl oxalate.

In 1929, Staudinger (272) reported the fractionation of polyanethole with ethyl ether, and in another paper (269) that of polyindene with petroleum ether or ethyl ether; the ether-insoluble portion was extracted with boiling cyclohexane, and this solution fractionated by precipitation with methanol.

Zhukov *et al.* (306) in 1935 obtained various fractions of sodium bivinyl polymers by means of petroleum ether, benzene, and chloroform.

C. ULTRACENTRIFUGATION

An ultracentrifuge is an instrument in which sedimentation in centrifugal fields can be measured quantitatively; the centrifugal fields employed are often quite strong, and the apparatus for producing them is rather complex. There are several types of ultracentrifuge in existence, but the earliest and still the best is that developed by Svedberg.

An ultracentrifuge can be used in two different ways: (*1*) to measure sedimentation velocity, that is, the rate of settling of a particle in a given centrifugal field, under standard conditions; (*2*) to measure sedimentation equilibrium, that is, the concentration gradient when equilibrium between sedimentation and diffusion has been established. Method 2 is used for molecular-weight determinations on high polymers; method 1 can be used for molecular-weight determinations also, but its chief value is for the measurement of heterogeneity or polydispersity.

It is obvious from Stokes' law that sedimentation velocity under gravity depends on particle size; the same is true in a centrifugal field, except that the applied force, and therefore the actual velocity, can be controlled, and made large enough to apply to particles of colloidal dimensions. When a strong centrifugal field is applied to a colloidal or a high-polymer solution, which is monodispersed with respect to particle size, the particles will all settle at the same rate; the boundary between solution and pure solvent will move outward from the centre of rotation, and remain sharp (except for slight spreading due to diffusion). In a polydispersed solution, however, the particles will settle at different rates, according to their sizes, and the boundary will spread more and more as it moves down. The amount of spread of the boundary (the concentrations across it are measured by suitable optical means while rotation continues) is a measure of the heterogeneity of the sample; the distribution curve can be obtained by differentiating the curve representing the relationship between the concentration and the distance from the centre.

Evidently, then, the ultracentrifuge furnishes not a preparative, but an analytical, method of fractionation. However, as an analytical method, it is probably one of the best available; Carothers (50), Dostal and Mark (70), Kraemer (149), Mark (176), and Staudinger (268) all recommend it. Kraemer (149) considers fractionation (by solubility methods) far too ineffective and laborious as compared to ultracentrifuge techniques; but the fact remains that an ultracentrifuge is a very complex and specialized piece of equipment, which not every laboratory can obtain. Unlike the above authors, Blease and Tuckett (38) regard fractionation methods as superior to the ultracentrifuge for obtaining distribution curves; they point out how insufficient is the number of ultracentrifuge measurements on record, and emphasize the fact that the validity of the few that there are has been questioned.

Most of the ultracentrifuge measurements on linear high polymers (this does not include the proteins) have been made by Kraemer (148–151). In 1932, Kraemer and Van Natta (151) measured the molecular weights of poly-ω-hydroxydecanoic acids, and found them reasonably, though not entirely, uniform. Later, Kraemer (148, 150) made measurements on cellulose and its derivatives. He pointed out that with the ultracentrifuge, the molecular distribution in cellulose can be easily measured (in cuprammonium) without any of the difficulties experienced in fractionation. His measurements showed that cellulose is continuously heterogeneous or, in other words, that all the members of the homologous polymeric series within a certain range are present. Actually, the calculation of the complete molecular-weight distribution is difficult, and Kraemer proposed the use of the average molecular weight together with a "non-uniformity coefficient" which he defined.

Kraemer's results are in contradiction to those of Stamm (265, 266), who in 1930 had found cellulose to be almost monodispersed, with only a very small proportion of much smaller particles.

Signer and Gross (257, 258) in 1934 performed ultracentrifuge measurements on polystyrene. They encountered a difficulty due to the "matting" of the molecules, that is, chain entanglements preventing the molecules from acting independently. (This difficulty is analogous to that met with in fractional precipitation, when precipitation "en bloc" occurs.)

Lamm (160) in 1934 used the ultracentrifuge to separate starch into two components, corresponding roughly to amylose and amylopectin; each was in turn found to be heterogeneous, especially the amylopectin.

Sebrell (256) mentioned that molecular-weight-distribution measurements by ultracentrifuge on Buna S had been made in the du Pont laboratories, but did not give any details. Scatchard *et al.* (237) in 1944 applied ultracentrifuge measurements to gelatin.[16]

D. CHROMATOGRAPHIC ADSORPTION

Chromatographic adsorption is a useful method for separating mixtures into their components; even closely related substances have often been successfully separated. The method consists in filtering the solution containing the mixture to be separated through a column of an adsorbent, "developing" the chromatogram by washing with pure solvent (this helps to separate the bands further), and eluting various parts of the column separately to recover the adsorbed material. The principle on which the separation is based is preferential adsorption; the components preferentially adsorbed are found in the upper part of the column, those more poorly adsorbed in the lower part, those most poorly adsorbed in the filtrate. Elution reverses the process of adsorption, that is, it causes the substance to pass from the adsorbed layer into solution again; it can be carried out either by filtering the elutant through the column and collecting the filtrates in a series of containers as the bands are washed out of the column one by one, or by dividing the column into bands and eluting each separately. The process received the name "chromatographic" adsorption because of the fact that most substances separated in this way are colored, and the bands in the column are visible; it is possible, however, to separate colorless substances, determining the position and width of the bands by other means, or simply dividing the column arbitrarily into several parts.

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[16] For a survey of ultracentrifuge methods and results on high polymers, see Kraemer (6).

Unlike mixtures usually chromatographed, which contain several distinct components, heterogeneous high polymers are continuous mixtures of members of a homologous polymeric series; it is too much to hope to separate each molecular species out of such a mixture. It has been found, however, that the smaller molecules are preferentially sorbed, and that fractionation is therefore possible. The chromatogram is colorless, and as there are no discontinuous bands, but rather a gradual transition from lower to higher fractions, the column is usually divided into an arbitrary number of parts, depending on the number of fractions desired.

The first study of this process as applied to the fractionation of high polymers was made in 1936 by Mark and Saito (179). In an attempt to fractionate cellulose acetate, they tested blood charcoal, aluminum oxide, calcium carbonate, and starch as adsorbents, and acetone and dioxane as solvents; they chose blood charcoal as adsorbent, acetone as solvent, and dioxane as elutant. The process, as finally worked out was as follows· A brass wire net was inserted into a glass tube 3 cm. in diameter and 42 cm. long and filled with three layers of powdered blood charcoal (10 g. each), on top of a bottom layer of glass wool and asbestos; the layers were separated from each other by round pieces of cloth. Three hundred cubic centimeters of a 0.5 per cent solution of cellulose acetate in acetone was filtered through this column under pressure; the chromatogram was washed with acetone, and the filtrate and washings collected. Each layer of charcoal was then dried, well shaken with 50 cc. of dioxane, and after standing for 1 day separated from the solution by filtration through glass wool, asbestos, and starch. The eluate was evaporated at 60°C., and the residue dried. The resulting fractions were found to differ in molecular weight (determined viscometrically), but not in acetyl content.

Loughborough and Stamm (167), in 1936, claimed that fractionation (with respect to molecular weight) of lignin was impossible by filtration through activated charcoal. However, in 1937 Levi and Giera (163) successfully repeated the experiments of Mark and Saito. They found that cellulose diacetate could be chromatographically fractionated; however, with cellulose triacetate, although adsorption is of the same order of magnitude, no fractionation took place. They explained this by assuming that the original cellulose is homogeneous, as is also the triacetate prepared from it, but in the transition from the triacetate to the diacetate, partial depolymerization takes place, resulting in heterogeneity; this would invalidate all methods of fractionating cellulose which depend on acetylation. They also recommended the use of 2:1 ether–alcohol as a solvent for the chromatographic fractionation of cellulose nitrate, with blood charcoal as adsorbent. In 1938, Levi *et al.* (164) compared these chromatographic experiments with fractional precipitation methods; they found an agreement for the cellulose diacetate, but the triacetate could be fractionated by precipitation, while it could not by chromatographic adsorption; they explained this by assuming degradation during precipitation, and particularly during the drying of precipitates.

Cajelli (48) in 1939 described a fractionation of rubber by chromatographic adsorption. Two hundred fifty cubic centimeters of a 0.5 per cent solution in 80:20 benzene–alcohol (95 per cent) was chromatographed in 30 g. of dried animal charcoal; this was washed with the same solution of benzene and alcohol. The charcoal was divided into three approximately equal parts, and each was Soxhlet-extracted with a 50:50 carbon disulfide–carbon tetrachloride solution. After partial evaporation of the resulting solutions at room temperature under vacuum, the viscosities were measured and found to differ.

E. ULTRAFILTRATION

It is often possible to separate particles of different sizes by ultrafiltration through carefully graded cellulose or nitrocellulose membranes. This separation is based on sieving action; the pore sizes are chosen in such a way that particles up to a certain size can pass, but larger ones cannot. This is satisfactory enough with spherical particles, even though complications may occur when the membrane interacts with the solution and passage through the membrane takes place in ways other than by sieving action. But linear particles, such as the high-polymer molecules, even though of colloidal dimensions in one direction, are of molecular dimensions in the other; as long particles have the same width as short ones, they should find it equally easy to pass through the pores of the membranes. However, because of the coiling up of the chains, and internal Brownian motion, long molecules may find it more difficult to pass through the tortuous passages than shorter ones would.

Ultrafiltration has been used with success for the fractionation of cellulose derivatives (35, 36, 47, 73, 74, 153). The method was applied to nitrocellulose by Kumichel (153) in 1928 and by Duclaux and Nodzu (73) in 1929, and to cellulose acetate by Caille (47) in 1931. Many others reject it as too slow, and Meyer (12) considers it unsatisfactory for chain polymers.

F. MOLECULAR DISTILLATION

This last method to be discussed is useful more for the purification of a high polymer (that is, the removal of low-molecular-weight material) than for the separation of high-molecular-weight fractions. In any polymerization or polycondensation reaction, however, molecules all the way from unreacted monomer up to those in the high-molecular-weight range are formed, and, in a sense, the removal of the low-molecular-weight material is a fractionation.

Molecular distillation is essentially a distillation at very low pressure, 10^{-3} or 10^{-6} mm. of mercury. The distance between the distilling pan and the collecting plate is shorter than the mean free path of the evaporating molecules, so that they suffer (on the average) no collisions while in the vapor state. Under these conditions, even very slightly volatile substances can be distilled without decomposition. Moreover, the diffusion velocity of a molecule is inversely proportional to the square root of the molecular weight, so that the lighter molecules distil off first, leaving the residue purified. Even very similar molecules or atoms (homologues or isotopes) can be separated.[17]

Bailey (29) in 1940 used molecular distillation to prove the heterogeneity of lignin. He used temperatures of 75–80°C. and a pressure of 10^{-3} mm. of mercury, and in some cases a temperature of 220°C. and a pressure of 10^{-6} mm. of mercury. He found a difference in the methoxyl content of the fractions.

III. CONCLUSION

Many methods have been used for the fractionation of high-polymeric substances, but some are much more generally useful than others. In order to make this review as helpful as possible, an attempt has been made to mention all the applications of fractionation techniques described in the literature up to the end of 1944.[18] There is no doubt that a few have been missed, but nevertheless the relative amount of space devoted to each method should be a good measure of its popularity. It is evident at once that solubility methods have been much the most frequently used. Of these fractional precipitation, in spite of disadvantages which have frequently been emphasized, is still the most popular, and fractional solution is its closest rival. The general preference for these methods is understandable, for they are relatively convenient, adaptable, versatile, and inexpensive. They are not, however, adequate for all needs.

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[17] See Mark and Raff (10) for a diagram and description of the apparatus. For a survey of various forms of molecular-distillation apparatus see Hickman (Chem. Rev. **34**, 51–106 (1944)).

[18] Since this time other papers dealing with fractionation have, of course, been published. No thorough search for them has been made, but the reader might appreciate having his attention called to the contributions to the theory of fractionation of Scott (and Magat) (J. Chem. Phys. **13**, 172–7, 178–87 (1945)) and of Zimm (Polymer Bull. **1**, 53–9 (1945)); to the discussions of analytical methods in papers by Morey and Tamblyn (J. Applied Phys. **16**, 419–24 (1945)), Doty, Zimm, and Mark (J. Chem. Phys. **13**, 159–66 (1945)), Boyer and Heidenreich (J. Applied Phys. **16**, 621–39 (1945)), and Stern, Senger, and Davis (Polymer Bull. **1**, 31–9 (1945)); and to the studies of preparative methods described by Howlett and Urquhart (Shirley Institute Memoirs **19**, 79–102 (1945)), Tamblyn, Morey, and Wagner (Ind. Eng. Chem. **37**, 573–7 (1945)), Badgley, Frilette, and Mark (Ind. Eng. Chem. **37**, 227–32 (1945)), Hauser, le Beau, and Shen (Rubber Age (N. Y.) **58**, 59–65 (1945)), Morey and Tamblyn (J. Phys. Chem. **50**, 12–22 (1946)), and, in a series of papers on fractionation by coacervation, by Dobry, Gavoret, and Duclaux (J. chim. phys. **42**, 41–4, 92–7, 109–13 (1945)).

Other methods, some of them demanding special techniques and elaborate apparatus, have been devised and found to possess peculiar advantages. When these methods are further improved and other new ones are developed (as they will be), the solubility methods may well lose their present favored position. In particular, it may be safely predicted that less tedious methods will be worked out for obtaining a knowledge of the distribution of molecular weights in a polymer. In the meantime, however, it is still true that in selecting a method for a given fractionation, precipitation or solution should first be considered; if these well-developed techniques prove unsuitable, another method may then be adapted to the particular problem in hand.

Although further advances in the techniques of fractionation may confidently be expected, so much experience has already accumulated that there is now little excuse for neglecting this essential part of the study of a high-polymeric system. If future investigators in the field of high polymers are careful to work with samples that are either homogeneous (monodispersed) or of known heterogeneity, their conclusions will be much more valid than are those in much of the earlier literature.

IV. SUMMARY

Methods that have been used for the fractionation of natural and synthetic high polymers (other than the globular proteins) have been discussed, as follows: fractional precipitation, fractional solution, differential rate of solution, ultracentrifugation, chromatographic adsorption, ultrafiltration, and molecular distillation. A review of the literature to the end of 1944 has been made; and the applications of the various methods have been described in the text and summarized in separate tables.

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FUNDAMENTAL PRINCIPLES OF CONDENSATION POLYMERIZATION

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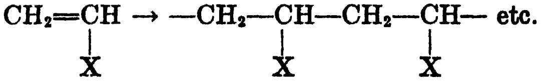
I. INTRODUCTION

In the opening paper (5) of his monumental series of pioneering investigations into the nature of polymeric substances, Carothers introduced a classification of polymer types which has proved to be extremely useful. After suggesting that the characteristic structural feature of high-polymer molecules is the existence of a structural unit —R—, repetition of which describes the entire molecule

—R—R—R— etc.

aside from modification of the terminal units of the chain, he clearly distinguishes two types of polymers: (*1*) *addition polymers*, in which the molecular formula of the structural unit —R— is identical with that of the monomer from which the polymer is formed, and (*2*) *condensation polymers*, in which the structural unit lacks certain atoms present in the monomer from which the polymer is formed or to which it can be degraded by chemical means.

The most important class of addition polymers are formed from unsaturated monomers



$$\mathrm{CH_2{=}\underset{\overset{|}{X}}{CH}} \rightarrow \mathrm{-CH_2-\underset{\overset{|}{X}}{CH}-CH_2-\underset{\overset{|}{X}}{CH}-}\ \text{etc.}$$

where X may be phenyl, halogen, acetoxy, etc. The molecular formula of the polymer is x times the molecular formula of the monomer. Condensation polymers are formed from monomers bearing two or more reactive groups of a character such that they may condense intermolecularly with the elimination of a by-product, usually water. As an example, polyesters are formed from hydroxy acids by intermolecular esterification.

$$x\mathrm{HO{-}R{-}COOH} \rightarrow \mathrm{HO{-}[R{-}COO]_{x-1}{-}R{-}COOH} + x\mathrm{H_2O}$$

The molecular formula of the polymer in this case is not an integral multiple of the formula of the monomer.

A number of representative condensation polymerizations are shown in table 1. This list is by no means exhaustive, but it indicates the variety of condensation reactions which have been employed in the synthesis of polymers. Cellulose and proteins come within the definition of condensation polymers on the grounds that they can be degraded, hydrolytically, to monomers differing from the structural units by the addition of the elements of a water molecule, although they have not been synthesized as yet by condensation polymerization. This is denoted by the direction of the arrows in the table, indicating depolymerization rather than the reverse.

From the point of view of the scientific investigator, perhaps the most significant feature of condensation polymerization is the commonplace nature of the chemical reactions involved. The knowledge available from the established organic chemistry of most of these reactions provides the basis for accurate predictions concerning the essential structural features of the products obtained. Quoting from the concluding remarks of Carothers' initial paper (5) on the theory of condensation polymerizations:

> "C [condensation] polymerization merely involves the use in a multiple fashion of the typical reactions of common functional groups. Among bifunctional compounds these reactions may proceed in such a way as to guarantee the structure of the structural unit, —R—, in the polymer, $(\text{—R—})_n$, formed. It is one of the immediate objects of the researches to be described in subsequent papers to discover how the physical and chemical properties of high polymers of this type are related to the nature of the structural unit."

These statements were made when synthesis of high polymers by intermolecular condensation appeared to be little more than a postulated possibility.

Condensation polymerization offers the possibility of constructing high-polymer molecules of accurately known structure. Furthermore, the average molecular weights of condensation polymers can be controlled at will by suitably varying the degree of condensation, and their average molecular weights often can be precisely determined by end-group titration. For these reasons condensation polymers are preferred subjects for fundamental investigations. At the present time, owing in large measure to the work of Carothers and his collaborators, the underlying principles of condensation polymerization are established, and condensation polymers are amenable to exact scientific interpretation. Condensation polymerization has passed beyond the empirical stage.

II. TYPES OF CONDENSATION POLYMERS

From the examples in table 1 it is clear that almost any condensation reaction can be utilized for the production of polymers. The primary requisite is a monomer, or pair of monomers, bearing two or more condensable functional groups. (A monomer such as formaldehyde can be regarded as bifunctional on the grounds that it is capable of forming two bonds with other units.) The products of these reactions are termed polyesters, polyamides, polyethers, etc., depending upon the inter-unit linkage, or upon the reaction involved: esterification, amidation, etc. In other cases it is necessary to use a less concise name, e.g., phenol–aldehyde, or urea–aldehyde, where chemical nomenclature provides no more suitable term.

Cutting across these various chemical types, two classes of condensation polymers are clearly distinguishable: linear polymers formed from reactants which are exclusively bifunctional, and non-linear polymers formed from reactants, some of which are trifunctional or higher (7). Polyesters from hydroxy acids or from glycols and dibasic acids are representative linear condensation polymers; those from glycerol and dibasic acids are three-dimensional. This distinction is warranted both by the structures of the two types of polymers and by their divergent properties.

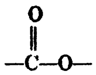
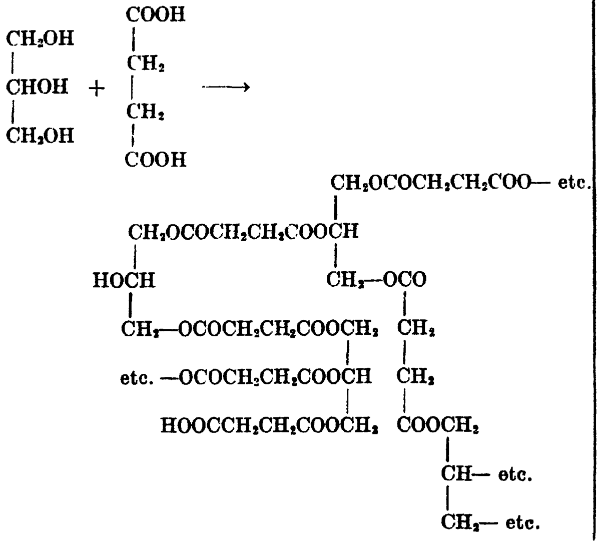
Bifunctional condensation, according to the very nature of the process, necessarily leads to *linear* products of *finite* molecular weight. In view of the impossibility of forcing the condensation reaction to completion, there will always be some few unreacted functional groups. These mark the ends of the linear molecules, which therefore are finite in length.

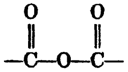
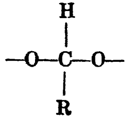
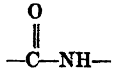
Linear condensation polymers are soluble in suitable solvents. On account of the regularity of structure, they usually occur in crystalline form. They are fusible, except when the melting point of the crystalline polymer lies above the decomposition temperature.

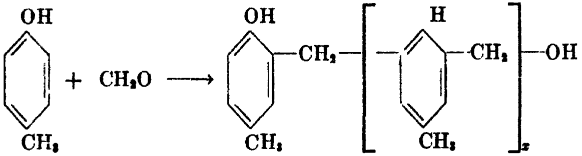
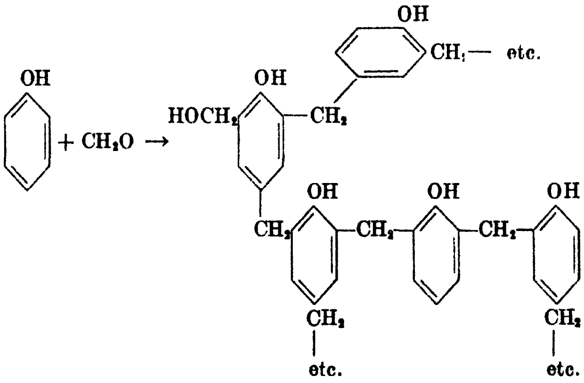
Non-linear, or three-dimensional, polymerizations are not restricted to growth in two directions only. It is at least conceivable that some of the molecules formed from reactants of functionality greater than two under proper conditions may be indefinitely large. This can be seen from the structure indicated in table 1 for the product from glycerol and succinic acid. As the polymer molecule increases in size its functionality increases, in contrast to the linear polymers prepared from bifunctional monomers, which always carry two functional groups. Although some of these terminal functional groups of the three-dimensional polymer may remain unreacted, others will combine, thus continuing the structure.

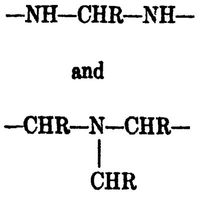
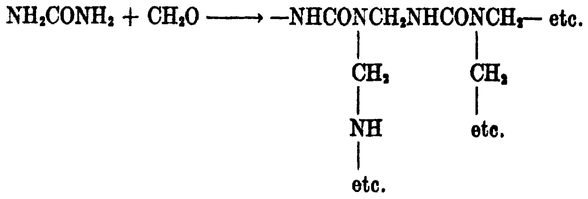
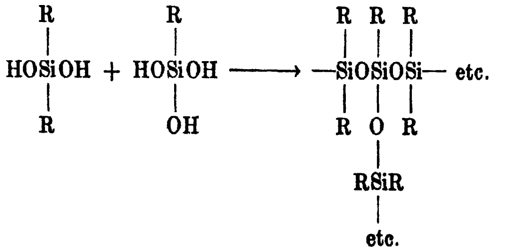
TABLE 1

Representative condensation polymers and their properties

TYPE	INTER-UNIT LINKAGE	EXAMPLES	MELTING POINT	CHARACTERISTICS	REFERENCES
			°C.		
Polyester	 $-\overset{\overset{\displaystyle O}{\parallel}}{C}-O-$	$HO(CH_2)_9COOH \longrightarrow HO-[(CH_2)_9COO]_x-H$	76	Hard; fibers cold draw above M.W. = 9000	(6, 19)
		$HO(CH_2)_2O(CH_2)_2OH + HOOC(CH_2)_4COOH \longrightarrow HO-[(CH_2)_2O(CH_2)_2OCO(CH_2)_4COO]_x-H$	Non-crystalline	Viscous liquid to glass-like; no fibers	(28)
		$HO(CH_2)_{10}OH + HOOC(CH_2)_4COOH \longrightarrow HO-[(CH_2)_{10}OCO(CH_2)_4COO]_x-H$	77	Hard; fibers cold draw above M.W. = 10,000; good strength	(6, 10, 28)
			Non-crystalline	Except at rather low extents of reaction, polymers are insoluble and infusible; no fiber properties; moderate strength	(54)

Polyanhydride.......	 $-\overset{O}{\overset{\Vert}{C}}-O-\overset{O}{\overset{\Vert}{C}}-$	$HOOC(CH_2)_8COOH \longrightarrow HO-[CO(CH_2)_8COO]_x-H$	83	Similar to crystalline polyesters; fibers cold draw at high molecular weight; very sensitive to water	(48)
Polysulfides	$-S-$	$ClCH_2CH_2Cl + Na_2S \longrightarrow Cl-[CH_2CH_2S]_x-Na$	Crystalline		(70)
	$-S-S-$	$HSCH_2CH_2SH + [O] \longrightarrow HS-[CH_2CH_2SS]_x-CH_2CH_2SH$	*ca.* 130	Crystalline	(70)
	$-\overset{S}{\overset{\Vert}{S}}-\overset{S}{\overset{\Vert}{S}}-$	$ClCH_2CH_2Cl + Na_2S_4 \longrightarrow Cl-[CH_2CH_2\underset{S}{\underset{\Vert}{S}}-\underset{S}{\underset{\Vert}{S}}]_x-Na$		Rubber-like; becomes crystalline only on stretching	(70)
Polyacetals..	 $-O-\overset{H}{\overset{\vert}{\underset{R}{\underset{\vert}{C}}}}-O-$	$HO(CH_2)_{10}OH + CH_2(OBu)_2 \longrightarrow$ $HO-[(CH_2)_{10}OCH_2O]_x-(CH_2)_{10}OH$	*ca.* 60	Fiber-forming at high molecular weight	(50)
Polyamides	 $-\overset{O}{\overset{\Vert}{C}}-NH-$	$NH_2(CH_2)_5COOH \longrightarrow H-[NH(CH_2)_5CO]_x-OH$	205	Fibers cold draw above about M.W. = 8000; high strength	(8, 15, 86)
		$NH_2(CH_2)_6NH_2 + HOOC(CH_2)_4COOH \longrightarrow$ $H-[NH(CH_2)_6NHCO(CH_2)_4CO]_x-OH$	260	Similar to the above	(9)

		EXAMPLES	MELTING POINT	CHARACTERISTICS	REFERENCES
			°C.		
Silk fibroin	$\overset{O}{\|}$	NH_2CH + $NH_2CHRCOOH \longleftarrow$ $—[NHCH_2CONHCHRCO]_x—$	Infusible without decomposi tion	Crystalline; good strength	
Cellulose	C—O--C	$H_{12}O_6 \longleftarrow —[C_5H_{10}O.$ C_6H $O—$ ɜ.	Infusible without compos tion	Crystalline; excellent strength when highly oriented	
Phe dehyde	CHR		Non-crysı line	Viscous, soluble, thermoplastic	(25)
			Non-crys' line	Sets to an insoluble, infusible resin	(55, 66)

Urea-formaldehyde..	 $-NH-CHR-NH-$ and $-CHR-\underset{\underset{CHR}{\vert}}{N}-CHR-$	 $NH_2CONH_2 + CH_2O \longrightarrow -NHCO\underset{\underset{\underset{\underset{\text{etc.}}{\vert}}{NH}}{\vert}}{\underset{CH_2}{\underset{\vert}{N}}}CH_2NHCO\underset{\underset{\underset{\text{etc.}}{\vert}}{CH_2}}{\underset{\vert}{N}}CH_2-\text{ etc.}$	Non-crystalline	Infusible, insoluble	(52, 67)
Polysilicones. . ..	Si—O—Si	 $HO\overset{\overset{R}{\vert}}{\underset{\underset{R}{\vert}}{Si}}OH + HO\overset{\overset{R}{\vert}}{\underset{\underset{OH}{\vert}}{Si}}OH \longrightarrow -\overset{\overset{R}{\vert}}{\underset{\underset{R}{\vert}}{Si}}O\overset{\overset{R}{\vert}}{\underset{\underset{\underset{\underset{\underset{\text{etc.}}{\vert}}{RSiR}}{\vert}}{O}}{\vert}}{Si}}O\overset{\overset{R}{\vert}}{\underset{\underset{R}{\vert}}{Si}}-\text{ etc.}$	Non-crystalline	Oils, greases, to hard thermosetting compositions; resistant to high temperatures	(53, 74)

To look at the situation in another way (7), consider the condensation of 2 moles of glycerol with 3 moles of succinic acid. Each ester group formed decreases by one the number of molecules present, excluding from consideration reactions between two functional groups on the same polymer molecule. Thus, if 5 moles of ester groups are formed intermolecularly, all of the units will be combined into one molecule. But there were initially 6 moles each of hydroxyl and carboxyl groups. Hence, if five-sixths, or 83.4 per cent, of the functional groups were esterified intermolecularly, all units would be combined into a single molecule and, incidentally, any further reaction would of necessity be intramolecular. It would be impossible for the intermolecular reaction to reach this stage without producing structures which assume macroscopic dimensions (7). Macroscopic structures may appear at earlier stages in the condensation. The above argument merely fixes a stoichiometric upper limit.

This calculation is presented to show that condensations of monomers having functionality greater than two should be expected to yield indefinitely large polymer structures at sufficiently advanced stages of the process. These "indefinitely large" or "macro" structures will extend throughout the volume of the polymerized material. Ordinarily their sizes, which will depend on the size of the polymerized sample as well as on the extent of reaction, can conveniently be expressed in grams. On the molecular-weight scale they may be considered as essentially infinite in size.

Among the physical characteristics of three-dimensional condensation polymerizations, the occurrence of a sharp gel point is of foremost significance. At the gel point, which occurs at a well-defined stage in the course of the polymerization, the condensate transforms suddenly from a viscous liquid to an elastic gel. Prior to the gel point all of the polymer is soluble in suitable solvents, and it is fusible as well. Beyond the gel point it is no longer fusible to a liquid nor is it entirely soluble in solvents.

Quite naturally these characteristics have been attributed to the restraining effects of three-dimensional network structures of "infinite" size within the polymer. This is the feature which distinguishes three-dimensional from linear polymers. It could be added that, owing to the greater irregularity of the three-dimensional polymers, generally they are not crystalline. Exceptions are found where the proportion of multifunctional units is small; e.g., in polymers of decamethylene glycol with adipic acid and a very small proportion of tricarballylic acid.

It is possible, of course, to avoid gelation in three-dimensional polymerizations by limiting the extent of esterification or by using proportions of reactants far from the amounts required stoichiometrically. For example, a mixture of 4 molecules of glycerol and 3 of succinic acid will not gel, regardless of the extent of esterification. But the product so obtained bears little resemblance to a linear condensation polymer; its molecular weight is low and its physical properties are inferior. Although these systems containing reactants of higher functionality do not necessarily lead to gelation, their properties nevertheless justify their consideration apart from linear polymers.

III. REACTIONS OF BIFUNCTIONAL COMPOUNDS

A. Characteristics of condensation polymerizations as compared with vinyl-type addition polymerizations

The distinction between condensation and addition polymers, as introduced by Carothers, is based upon the relationship between the compositions of the structural unit and of the monomer. This basis for differentiation is both convenient and appropriate, although whether or not the polymer is of the same empirical composition as the monomer is, in itself, of trivial importance. Justification for this distinction is found in the striking differences between the characteristics of the polymerization *processes*, rather than in the nature of the products.

Addition polymerizations of unsaturated monomers generally proceed by a chain mechanism. Primary activation of a monomer M (or possibly a dimer) is followed by the addition of other monomers in rapid succession until the growing chain eventually is deactivated, with the net result that a polymer molecule, M_x, has been formed from x monomers. The entire synthesis of an individual polymer molecule from unreacted monomers occurs within a brief interval of time—often within a few seconds—whereas the over-all conversion of monomer to a good yield of polymer may require hours. Thus, at any instant during the polymerization process the reaction mixture consists almost entirely of unchanged monomer and of high polymer. Material at intervening stages of growth is virtually absent; the portion consisting of actively growing chains is so small as to be immeasurable by ordinary chemical methods. As the per cent conversion to polymer increases, the average degree of polymerization of the polymerized portion remains approximately the same, or at least does not change commensurately with the extent of conversion to polymer.

$$M \xrightarrow{\text{activation}} M^* \xrightarrow{+M} M_2^* \xrightarrow{+M} M_3^* \longrightarrow \text{etc.}$$

The above characteristics of vinyl addition polymerizations follow naturally from the fact that they are chain reactions in the kinetic sense of the term. As such their reaction mechanisms are complex, and the structures of the polymeric products are sometimes difficult to establish with certainty.

Condensation polymerizations, considered from a general point of view, might appear to be even more complex. To consider the polyesterification of a hydroxy acid, for example, the first step is intermolecular esterification between two monomers, with the production of a dimer.

$$\text{HORCOOH} + \text{HORCOOH} \rightarrow \text{HORCOORCOOH} + \text{H}_2\text{O}$$

This step may be followed by reaction of the dimer with another monomer to form a trimer, or the dimer may react with another dimer to form a tetramer, etc. These species in turn may react with monomers, dimers, etc. All of the reactions

$$x\text{-mer} + y\text{-mer} \rightarrow (x + y)\text{-mer}$$

in which x and y assume every possible combination of positive integral values, are to be reckoned with. Whereas in addition polymerization chain growth is ordinarily restricted to the addition of monomers to active chains, in condensation polymerization reactions between two polymer molecules occur as well.

If it were necessary to assign a separate rate constant, k_{xy}, to each of the above reactions occurring in condensation polymerization, kinetic analysis would be extremely difficult if not impossible. However, these various steps need not be differentiated. All involve the same process, e.g., esterification, and, as will be shown later, the rate constants for the various steps are approximately equal. Consequently, the entire polymerization process can be regarded as a reaction between functional groups, e.g., OH and COOH. The individual molecular species and the manifold of steps in which they are involved can be disregarded. This point of view having been adopted, the chemical reaction mechanism of polyintermolecular condensation is no more complex than the condensation of analogous monofunctional compounds. In polyesterification, for example, the rate of esterification is similar to the rate of reaction of ethyl alcohol with acetic acid under similar conditions, it is subject to acid catalysis in a parallel manner, etc. Similarly, the polyamidation reaction parallels closely the rate, temperature coefficient, and reaction order of monoamidations (*cf. seq.*). The essential differences lie only in the functionality of the reactants and the nature of the products produced.

Upon returning to the contrast between the mechanisms of addition and condensation polymerization, it should be noted that the synthesis of any given condensation polymer molecule is accomplished by a series of independent condensations which ordinarily occur at intervals scattered over the period during which the polymerization is carried out, and not during a single comparatively brief interval, as is the case in addition polymerization. Interruption of a linear, or bifunctional, condensation polymerization at an early stage of the process yields a polymer of low average molecular weight. Unless the average degree of polymerization is very low—less than about ten units—it will contain a negligible amount of monomer (less than 1 per cent). As the reaction is continued the low polymers first formed condense further, with the result that the average molecular weight continues to increase. The final molecular weight of a linear-condensation polymer is limited only by the attainable degree of completion of the condensation reaction, or by side reactions which may consume functional groups without producing inter-unit linkages. Thus, in condensation polymerization monomer disappears almost completely during the initial phase of the polymerization process, but in order to attain a high average molecular weight it is necessary to continue the polymerization until the reaction approaches closely to completion. In vinyl addition polymerization, on the other hand, high polymer makes its appearance at the outset, and the duration of the process is determined by the yield of polymer desired, and not by the molecular weight required. Addition-polymer molecules do not respond to further polymerization by inter-reaction with one another (with the exception of some diene polymers).

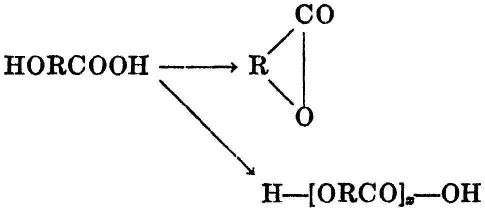
In principle, at least, many vinyl polymers could be synthesized by condensation processes. For example, ethylene can be *addition* polymerized (71) to a product which is essentially —$(CH_2)_n$—. A polymer of the same structure can be obtained by a Wurtz *condensation* of decamethylene dibromide (17):

$$Br(CH_2)_{10}Br + Na \xrightarrow{\text{ether}} H\text{—}[(CH_2)_{10}]_x\text{—}H$$

If other dibromides were used, it is conceivable that the chain structures of other vinyl polymers could be duplicated. However, such methods of synthesis are of no actual importance, and the above example merely emphasizes further that the essential differences between addition and condensation polymerizations occur in the processes of polymerization rather than in the character of the products.

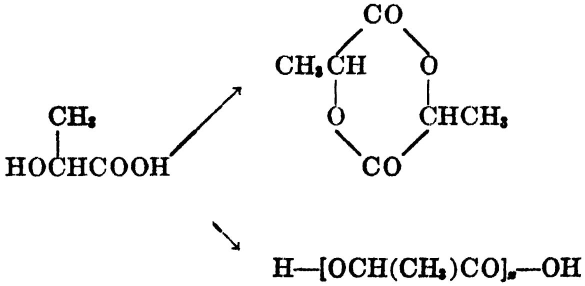
B. Ring formation vs. chain polymerization

Polyfunctionality of the reactants is not sufficient in itself to assure formation of polymer; the reaction may proceed intramolecularly with the formation of cyclic products. For example, hydroxy acids form either (or both) lactone or linear polymer



the direction of the reaction depending on the particular hydroxy acid and, to a lesser extent, on the reaction conditions.

α-Hydroxy acids, such as lactic acid, condense to give both the dimeric cyclic ester, lactide, and a linear polymer:



The condensation of amino acids likewise may produce cyclic and/or linear products; the same is true of virtually all polyfunctional condensation reactions.

The prime factor governing the course followed by a bifunctional reaction is the size of the ring (or rings) which can be obtained through intramolecular condensation. If the ring size is less than five atoms or more than seven, the product will consist almost entirely of open-chain polymer, under ordinary conditions. If a ring containing five annular atoms can be formed, this will be the product exclusively; if of six or seven atoms, either, or both, ring and chain polymer are likely to be formed. Larger rings are formed only under special conditions, e.g., by conducting the condensation at high dilution (75, 89) where opportunities for intermolecular reaction are less favorable, or by heating the polymer in vacuum in the presence of catalysts, the cyclic product being continually removed as it is formed through intramolecular cyclization (49, 50, 83, 84).

The observed dependence of ease of ring formation on ring size for cyclic esters and for cyclic anhydrides is shown in figure 1, taken from a paper by Spanagel and Carothers (83). This type of dependence is quite general, although it will differ in detail from one series to another.

The difficulty with which rings of less than five atoms are formed is readily explained by the strain imposed on the valence angles. Five-atom rings are virtually strainless (in a symmetrical five-atom ring the bond angle is 108°); in all larger rings valence-angle strain can be relieved entirely through the assumption of non-planar forms (Sachse–Mohr theory), except for such obstructions as may arise from steric interferences between substituents. Nevertheless, bifunctional condensations involving units of more than seven atoms do not ordinarily yield rings in appreciable quantity, and, as noted in figure 1, rings of about eight to twelve members are formed with considerable difficulty, even at high dilution or in a vacuum at elevated temperatures in the presence of a catalyst.

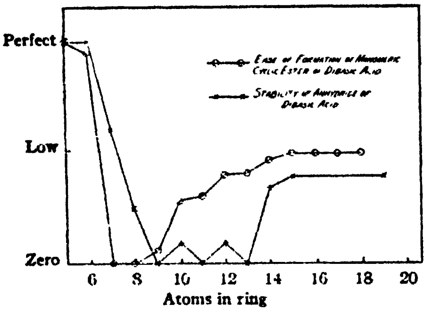


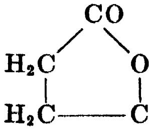
FIG. 1. Ease of formation and stability vs. ring size. (From Spanagel and Carothers (83).)

Carothers and coworkers (6, 16, 83) attributed this minimum in ease of ring formation to two factors: the statistical improbability of the relatively restricted configuration required for the formation of rings in this size range, and the interference, or repulsions, between the hydrogen atoms which necessarily become crowded together within such rings. Scale models of rings composed mainly of —CH_2— groups demonstrate the incidence of these factors. The interferences between the hydrogen atoms leave little freedom of choice in the configuration of the ring. Consequently, the formation of a ring from a bifunctional monomer in this size range will be statistically unfavorable; before such a bifunctional monomer may react intramolecularly, it must coil itself into a specific configuration, in contrast to the numerous other possible configurations available to it in any one of which intermolecular reaction is permissible.

In the scale models of these rings of eight to about twelve members it will be observed further that a number of the hydrogens are forced to occupy positions within the interior of the rings where they are crowded closely together. The domain of the hydrogen atom is ill defined but large. Repulsions between hydrogens extend beyond the kinetic theory radius of about 1.3 Å. Hence, in addition to the statistical improbability of ring configurations for monomers in this size range, they are also energetically unfavorable.

As the ring size is increased above fifteen atoms, the number of permissible ring configurations increases, and it is no longer necessary to crowd hydrogen atoms within the ring. The ease of ring formation increases in this range. However, in ordinary bifunctional condensations (no diluent) the primary product from monomers (or dimers) of fifteen or more members is almost exclusively linear polymer. This results from the statistical improbability that the ends of a long chain of atoms, connected by valence bonds about which there is free rotation, will meet. Although various stable ring configurations are possible for long chains, the total number of other configurations is disproportionately larger; the ring configurations represent but a small fraction of the total of all possible configurations. It can be shown from statistical considerations that the probability that the two ends of a long chain will occupy positions adjacent to each other varies approximately as the inverse three-halves power of the chain length (45, 60), or number of chain atoms. Hence, intramolecular reaction gradually becomes less probable as the length of the bifunctional chain increases. This argument finds further application in supplementing various experimental results which indicate that condensation polymers possess an open-chain rather than a macro-ring structure (6, 10, 12, 62).

The principles set forth above account reasonably well for the course pursued by bifunctional condensations under ordinary conditions and for the relative difficulty of ring formation with units of less than five or more than six or seven members. They do not explain the formation of cyclic monomers from five-atom units to the total exclusion of linear polymers. Thus (6), γ-hydroxy acids condense exclusively to lactones such as I, γ-amino acids give the lactams (II), succinic acid yields the cyclic anhydride (III), and ethylene carbonate and ethylene formal occur only in the cyclic forms IV and V.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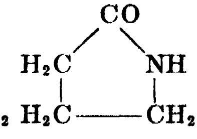
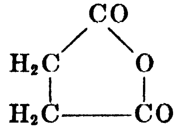

II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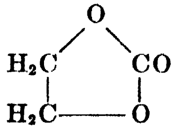
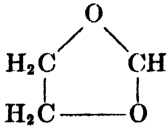

IV


V

Furthermore, formation of these products occurs with much greater ease than linear polymerization of units of six or more chain members, and they are more stable to hydrolysis or other ring-opening reactions.

The steric and configurational factors discussed above would suggest that five-membered rings should form somewhat more readily than rings of six or seven members, but they offer no explanation for the total exclusion of intermolecular condensation, nor do they explain the much greater rate of intramolecular reaction of five-membered units, as compared with the rates of intermolecular reaction of larger units. A possible partial explanation for these peculiarities of five-membered ring closure may be found from further consideration of hydrogen repulsions. In these rings the hydrogen atoms occur around the periphery; hence their mutual interactions are minimized. (In the open-chain planar zig-zag form each hydrogen atom, though slightly farther removed from its nearest neighbors, is surrounded by a greater number of near-neighbor hydrogen atoms than in the planar ring form.) It is doubtful, however, that this factor alone is responsible for the pronounced preference for the ring form which is observed for five-membered units.

Substitution of carbonyl, oxygen, or other atoms or groups for methylene should be expected to modify ring-forming tendencies. Valence angles and bond lengths are altered somewhat, but perhaps of greater importance is the decrease in the number of interfering hydrogens (16) as the methylene members are replaced. According to the present interpretation, a decrease in the proportion of methylene groups should diminish both the overwhelming tendency toward intramolecular reaction of five-membered units and the difficulty of forming rings of eight to twelve members. Other factors doubtless need to be considered as well.

Bifunctional monomers capable of forming six- or seven-membered rings condense variably, depending upon the particular monomer. The products normally obtained in the absence of diluent in various representative bifunctional condensations are listed in table 2 for unit lengths of six and seven members. The term "interconvertibility" refers to the reversible transformation between the ring and the linear polymer. Several of the six-membered units (table 2) prefer the ring form exclusively, but most of them yield both products, or, at least, they are readily interconvertible. Seven-membered units either yield linear polymers exclusively, or, if the cyclic momoner is formed under ordinary conditions, it is convertible to linear polymers.

C. Polymerization of cyclic compounds

The reversible transformation between rings of six members and the corresponding chain polymers occurs with remarkable ease (13). The six-membered cyclic esters, for example, polymerize spontaneously on standing even at room temperature (13). The polymers can be converted readily to the monomeric lactones by distillation. Thus, all of the processes indicated below

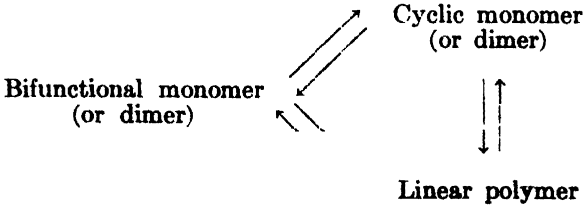
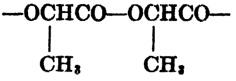
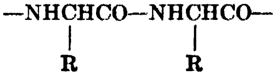


TABLE 2

Ring formation vs. chain polymerization from six- and seven-membered units

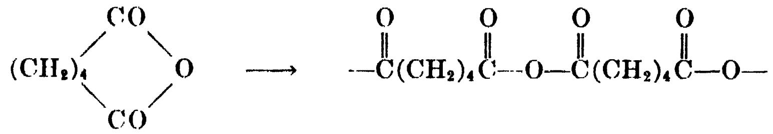
	STRUCTURAL UNIT	PRODUCTS OF BIFUNCTIONAL CONDENSATION	
		Six-membered unit	Seven-membered unit
ω-Hydroxy acid self ester......	$-O(CH_2)_nCO-$	Both ring and polymer spontaneously interconvertible (13)	Chiefly ring; interconvertible (91)
α-Hydroxy acid self ester......	 $-\mathrm{O}\underset{\mathrm{CH_3}}{\underset{\vert}{\mathrm{CH}}}\mathrm{CO}-\mathrm{O}\underset{\mathrm{CH_3}}{\underset{\vert}{\mathrm{CH}}}\mathrm{CO}-$	Linear polymer probably is the primary product (13, 22); interconversion is easy	
Alkylene carbonate............	$-(CH_2)_nOCOO-$	Both ring and polymer; easily interconvertible (13, 18)	Linear polymer only (18)
Dibasic acid anhydride.	$-(CH_2)_nCO-O-CO-$	Ring only	Linear polymer; convertible to ring (47)
Alkylene formal..	$-(CH_2)_nOCH_2O-$	Ring only (50)	Both ring and polymer; interconvertible (50)
Self amide of ω-amino acid ...	$-NH(CH_2)_nCO-$	Ring only (6)	Both ring and polymer (11); interconvertible at high temperatures
Self amide of α-amino acid.. .	 $-\mathrm{NH}\underset{\mathrm{R}}{\underset{\vert}{\mathrm{CH}}}\mathrm{CO}-\mathrm{NH}\underset{\mathrm{R}}{\underset{\vert}{\mathrm{CH}}}\mathrm{CO}-$	Ring usually predominates, but some linear polymer can be formed; interconversion is difficult	
Alkylene sulfide.	$-CH_2CH_2S-CH_2CH_2S-$	Linear polymer; converted with some difficulty to ring (63)	
Alkylene ether-sulfide........	$-CH_2CH_2O-CH_2CH_2S-$	Linear polymer (70)	

can be realized with most bifunctional monomers of six members and also with some of seven members. Dimers are mentioned in the above scheme in consideration of compounds such as α-amino acids and α-hydroxy acids, the dimers of which are equivalent to six-membered units. The mobility of the above transformation renders difficult a decision as to whether ring or polymer is the primary product of bifunctional condensation in the case of six-membered units (see table 2).

Carothers, Dorough, and Van Natta (13) have drawn attention to the parallelism between the ease of reversible polymerization of six-membered rings and their susceptibility to hydrolysis. No satisfactory explanation for their exceptional reactivity is apparent.

Larger rings, though difficult to form, are relatively stable with respect to polymerization (cyclic anhydrides excepted). However, at elevated temperatures, and preferably in the presence of a catalyst, they can be converted smoothly to linear polymers. Thus, the conversion of cyclic compounds to polymers is quite general (16) except, of course, with the more stable rings of five, and in a few cases six, members where the corresponding polymers are unknown. For example, ε-caprolactam (11, 79), polymethylene carbonates (49), macrocyclic esters (49), macrocyclic amides (44), and cyclic anhydrides such as adipic (47), to mention a few, can be converted to linear polymers under suitable conditions.

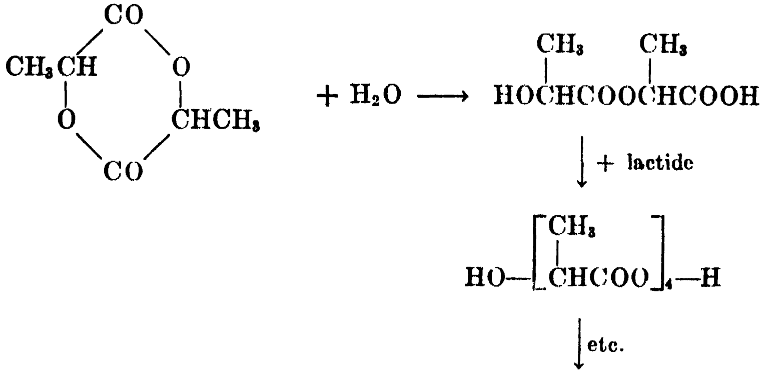
The products formed by polymerization of these rings are not ordinarily distinguishable from the polymers formed by direct condensation polymerization of the bifunctional monomers. Thus, spontaneous polymerization of adipic anhydride (47) gives a product which is identical in composition and in chemical and physical properties with the polymer produced by direct anhydridization of adipic acid. Literal adherence to definition would demand that the one be called an addition polymer and the other a condensation polymer, in spite of their possible identity.



$$\longrightarrow\ \text{—}\overset{\overset{\text{O}}{\|}}{\text{C}}(\text{CH}_2)_4\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—O—}\overset{\overset{\text{O}}{\|}}{\text{C}}(\text{CH}_2)_4\overset{\overset{\text{O}}{\|}}{\text{C}}\text{—O—}$$

The unequivocal distinction between the two types of *processes*, the one an addition and the other a condensation, by which these various polymers can be prepared cannot, and should not, be disregarded. However, designation of the product as an addition polymer in the one case and as a condensation polymer in the other would lead inevitably to confusion It is customary to consider polymers of this type as condensation polymers, regardless of their origin. This can be justified on the grounds that the same polymer may be formed by condensation, and it can be degraded, usually hydrolytically, to a monomer(s) differing in composition from the structural unit(s). On this basis the polymer comes within the original definition of condensation polymers.

The mechanism of the addition polymerization of ring compounds bears little resemblance to addition polymerization of vinyl monomers. They are not chain reactions. Usually they proceed by interchange reactions, induced either catalytically (49, 50, 79) or by the presence of small amounts of end-group-producing substances (13, 38). For example, the polymerization of lactide, the cyclic dimer of lactic acid, is accelerated by small amounts of water (3). The water undoubtedly hydrolyzes the lactide to lactyllactic acid, which may then react with other lactide molecules by ester interchange (38). The reaction scheme can be represented as follows:



Similarly, water accelerates the polymerization of ϵ-caprolactam (79), presumably *via* a similar mechanism:

$$\underline{NH(CH_2)_5CO} + H_2O \longrightarrow NH_2(CH_2)_5COOH$$

$$\Big\downarrow \text{+ cyclic monomer}$$

$$H—[NH(CH_2)_5CO]_2—OH$$

$$\Big\downarrow \text{etc.}$$

Strong acids or bases, which are sometimes used to catalyze these transformations (31, 38, 49, 50, 91), probably are effective because of their ability to accelerate the interchange reaction between a few end groups and the more abundant inter-unit linkages.

These processes resemble vinyl-type addition polymerizations only in that they proceed exclusively (as here represented) by addition of the monomer (or cyclic dimer) to linear chain molecules. They differ from vinyl polymerization in that the specific rate of the first step, ring opening, is comparable with the specific rate of succeeding monomer additions. Hence, the over-all polymerization process does not assume the characteristics of a chain reaction. Ring-chain polymerizations have not been investigated in detail, but according to the mechanism proposed the various chain molecules (initiated by hydrolysis in the above examples) should undergo more or less simultaneous growth throughout the course of the polymerization. At any intermediate stage of the polymerization the material should be separable into unchanged monomer and polymer. In contrast to vinyl polymerizations, however, as the polymerization is continued not only should the amount of polymer increase, but its average molecular weight should increase also.

IV. KINETICS OF CONDENSATION POLYMERIZATION

The similarities between polyfunctional condensations and the analogous monofunctional reactions were pointed out in the course of the above qualitative discussion of reaction mechanisms. They proceed under similar conditions of temperature and catalysis, their temperature coefficients are similar, etc. It was suggested that the maze of intermolecular reactions, involving molecules of every species in reactions with every other species, may be disregarded, and the entire process can be looked upon merely as a reaction between functional groups. To the extent that this rather sweeping assumption is justified, disappearance of unreacted functional groups must occur in a manner paralleling exactly the course followed by the analogous monofunctional reaction under the same conditions.

In opposition to the unqualified assumption that a polyfunctional reaction and the analogous monofunctional reaction proceed in a quantitatively equivalent manner, it has been held that the rate must necessarily be depressed by the high molecular weight of the intermediate products (which are also reactants) formed in the polyfunctional reaction (2, 6, 14, 23, 46, 64). Various arguments have been advanced in support of the contention that large molecules should be less reactive than smaller ones. The lower mobility of large molecules in the liquid state (23, 64) and the decrease in collision rate (in gases!) with increase in molecular weight are frequently cited as contributing to lower reactivity. The "steric factor" is supposed to be reduced, owing to shielding of the functional group within the coilings of the remainder of the molecule (23, 64). Even statistical mechanics has been invoked to derive (erroneously) a decrease in reactivity with size (2). Furthermore, as polymerization progresses the viscosity of the reaction medium increases rapidly. Dostal and Mark (24) suggest that this rise in viscosity should further depress the reaction rate. It would appear, in the face of the aggregate effects of these alleged obstacles, that the established synthesis of high polymers through condensation polymerization should have been a practical impossibility.

The principles of chemical reactivity as applied to large molecules will be examined first from a theoretical point of view in the paragraphs which follow. Experimental results bearing on the chemical reactivity of polymer molecules will then be presented in the remainder of this section of the paper and in the section which follows.

A. Theory of the reactivity of large molecules

At the outset it should be pointed out that the intrinsic chemical reactivity of a functional group should be essentially independent of the size of the molecule to which it is attached. The intrinsic chemical characteristics of a functional group may, to be sure, be profoundly altered by substitution in the molecule. However, the substituent is effective only when it is introduced near the functional group. If the point of substitution is removed from the functional group by more than five or six atoms, its effect is negligible. The reactivity of the carboxyl group of lactic acid probably is altered somewhat by esterification of its hydroxyl group with another molecule of the hydroxy acid, but addition of a third lactic acid residue scarcely can be expected to affect the reactivity of the terminal carboxyl group appreciably. Consequently, a change in the intrinsic chemical reactivity of the functional groups, if it occurs at all, will be confined to the early stages of the polymerization.

Arguments favoring a decrease in reactivity with molecular size usually have arisen from considerations of the mechanics of interaction of two functional groups attached to large molecules, rather than from any inherent abnormal character of the functional groups themselves. On account of the low mobility of polymer molecules, it has been concluded, for example, that the collision rate is correspondingly diminished. It is well established that large molecules diffuse slowly, but the collision rate of the functional group must not be confused with the diffusion rate for the molecule as a whole. The internal mobility with reference to motions of the terminal functional group will be much greater than the macroscopic viscosity would indicate. While its range of diffusion within an interval of time which is small compared to the period required for displacement of the molecule as a whole will be limited by its attachment to the polymer molecule, the terminal group may diffuse readily over a considerable region through rearrangements in the configurations of nearby segments of the chain. Its actual oscillations against its immediate neighbors may occur at a frequency comparable to, or at any rate not much less than, that prevailing in simple liquids. Thus the actual collision frequency will bear scant relationship to the mobility of the molecule as a whole or to the macroscopic viscosity.

Rabinowitch and Wood (73) have demonstrated in a particularly lucid way that a pair of neighboring molecules, or functional groups, in the liquid state may collide repeatedly before diffusing apart. The lower the diffusion rate the greater the prolongation of this series of encounters between functional groups, but it will be proportionately longer before the functional group diffuses to a new position in which it is again an immediate neighbor of another functional group. Another series of collisions will ensue, and this pair will be separated by diffusion of one of them, unless, of course, that exceedingly rare event, chemical reaction, occurs during one of the collisions. Thus, decreased mobility, due to large molecular size and/or to high viscosity, will alter the time distribution of collisions experienced by a given functional group, but it should not affect to any great extent the collision rate averaged over a period of time long compared with the interval required for diffusion from one partner to the next.

Even if this average collision *frequency* is diminished somewhat by a possible reduction in internal mobility as the polymerization progresses, the *duration* of the collided state will be prolonged proportionately. Hence, the concentration of pairs of functional groups sufficiently close together to permit the condensation reaction to occur (if the necessary energy is available) is independent of mobility. This conclusion can be established more rigorously by following Eyring's (26) theory of reaction rates. The transitory activated complex is defined by Eyring in such a way that its concentration can be expressed as if it were in chemical equilibrium with the reactants. Obviously, mobility within the liquid will not affect the equilibrium: reactants ⇄ activated complex. Since the rate of reaction is proportional to the concentration of activated complex, it will not be affected by the mobility of the molecules, the diffusion rate, or the viscosity.

Exceptions to these conclusions will occur when the molecular mobility is extremely low, i.e., when the molecular weight and the viscosity are extremely high, or when the specific reaction rate is unusually great and the mobility is low (73). If the reaction rate is too fast, or the mobility too low, to allow maintenance of the equilibrium concentration of reactant pairs in positions adjacent to one another in the liquid, then diffusion will become the rate-controlling step. It is unlikely that this will occur in ordinary condensation polymerizations even up to molecular weights and viscosities far in excess of those attained in the experiments described above. For example, in esterification (acid-catalyzed at around 100°C.) less than one collision in 10^8 between functional groups is fruitful in producing ester (51). Within the interval required for this number of collisions, appreciable diffusion of the molecule may easily occur.

In vinyl polymerizations the mobility of the monomer, even in the presence of much polymer, should be adequate to avoid dependence of rate on diffusion in spite of the rapidity of this reaction. The chain-termination step, involving interaction between the termini of two large molecules, occurs at a comparatively high percentage of encounters, i.e., the specific rate constant for this step is large. Here it is not improbable that low mobility may depress the rate of the termination reaction somewhat (thereby producing an acceleration of the polymerization rate in this case) when the viscosity of the system is not reduced through the use of a diluent.

In their recent book dealing with polymerization mechanisms Mark and Raff (64) have suggested further that a long-chain polymer molecule will tend to surround its terminal functional group in such a way as to shield it from contact with other molecules. On the contrary, there is no reason to suppose that a functional group will prefer to imbed itself in its own chain rather than among other similar polymer molecules present in the medium. The inter-twining chains merely act as so much diluent in the same way that ethyl acetate, for instance, acts as a diluent at advanced stages in the esterification of alcohol and acetic acid.

B. Experimental results on linear polyesterification

Experiments on the rates of esterification of polyfunctional and monofunctional reactants demonstrate clearly that, so far as the chemical inter-reaction between functional groups is concerned, mono- and poly-functional reactions are equivalent (28). In these experiments the reaction between precisely equivalent quantities of diethylene glycol and adipic acid, a dibasic acid, was followed by titration of total unreacted carboxyl groups in samples removed from the reaction mixture. The extent of reaction, *p*, defined as the fraction of the functional groups which have been esterified at the time of removal of the sample, was calculated from the titer. In the same manner diethylene glycol and caproic acid, a monobasic acid, were heated together at the same temperature and the reaction was followed similarly. In figure 2 $1/(1 - p)^2$,

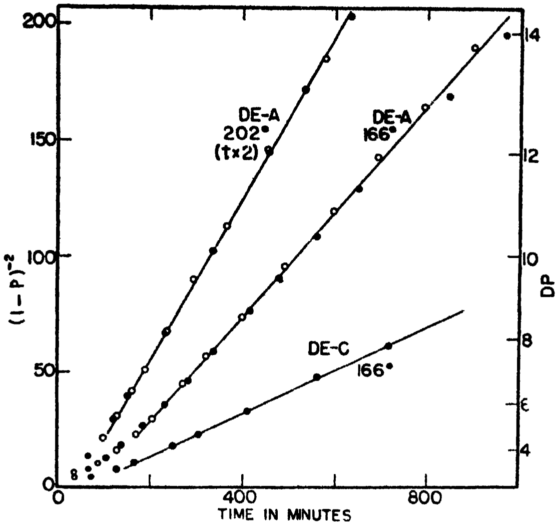


FIG. 2. Diethylene glycol–adipic acid (DE–A) and diethylene glycol–caproic acid (DE–C) reactions. Time values at 202°C. have been multiplied by 2. (From reference 28.)

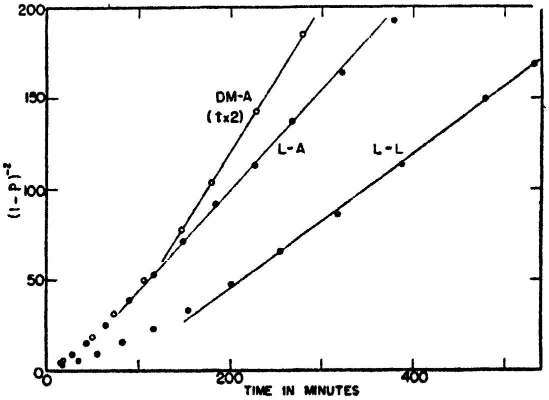


FIG. 3. Reactions of decamethylene glycol with adipic acid (DM–A), lauryl alcohol with adipic acid (L–A), and lauryl alcohol with lauric acid (L–L), all at 202°C. (from reference 28).

which is approximately proportional to the reciprocal of the square of the concentration of functional groups, is plotted against the time in minutes (28). Dots and circles are used to distinguish data from duplicate experiments. Similar results comparing the reactions of decamethylene glycol with adipic acid (bi-, bifunctional), lauryl alcohol with adipic acid (mono-, bifunctional), and lauryl alcohol with lauric acid (mono-, monofunctional) are shown in figure 3

(28). The degree of polymerization, $\overline{DP}_n$, or average number of units per molecule, is equal to $1/(1 - p)$, which is the square root of the ordinates in figures 2 and 3.

The reason for the choice of this particular mode of plotting the results (i.e., as a third-order reaction) will be discussed below. The point of importance here is the similarity of the courses followed by condensations producing polymers and those in which monofunctional reactants are involved. The monofunctional reactions actually are somewhat slower, but this is due principally to the greater equivalent weights of the initial monofunctional reactants, resulting in greater dilution of the functional groups with inert hydrocarbon chains. The curves for the mono- and the poly-functional reactions are superimposable by merely multiplying all time values for one of them by the same factor. If the functional groups in the poly-functional reaction became progressively less reactive as the reaction progressed and the average molecular size increased, this similarity with the monofunctional reaction would not have been observed.

As is well known, esterification reactions are catalyzed by hydrogen ions. In the absence of a strong acid catalyst a second molecule of the carboxylic acid undergoing esterification functions as catalyst. The rate, therefore, should be proportional to the product of the hydroxyl concentration and the square of the carboxyl concentration. When the concentrations, C, of the reacting groups are the same,

$$-\mathrm{d}C/\mathrm{d}t = kC^3$$

where k is the velocity constant. Upon integration this expression becomes:

$$2kt = 1/C^2 - \text{Const.}$$

If the reaction is uniformly third order from the beginning onward, the constant of integration will be $1/C_0^2$, where C_0 is the initial concentration. If the effect on concentration of the decrease in volume due to loss of water during the reaction is neglected, C may be replaced by $C_0(1 - p)$, and

$$2C_0^2kt = 1/(1 - p)^2 - \text{Const.} \tag{1}$$

The velocity coefficient k will be a constant only when the (average) reactivities of unreacted functional groups remain constant throughout the observed course of the reaction. If as the polyfunctional reaction progresses this reactivity is diminished, owing to the increased average size of the reacting species or to the decreased fluidity of the medium, k will not assume a constant value and, consequently, $1/(1 - p)^2$ will not increase linearly with t in accordance with equation 1.

During the initial portion of the esterification reactions shown in figures 2 and 3, equation 1 is not obeyed, as is shown by the curvature in these plots extending as far as about 80 per cent esterification corresponding to a $\overline{DP}_n = 1/(1 - p)$ of 5. This peculiarity has been attributed (28) to the rather pronounced change in characteristics of the reaction medium, particularly its dielectric properties. Whatever the cause of this behavior may be, it is typical of both mono- and poly-esterifications, and is not therefore in any way related to the sizes of the reacting molecules.

Beyond an average degree of polymerization of about 5 and as far as a *DP* of 14, the relationship becomes linear within experimental error. Straight lines have been drawn through the sets of points in figures 2 and 3 in this region. Here the reaction is evidently third order with a velocity coefficient, *k*, which is unaffected by the increasing average size of the reacting molecules.

Baker, Fuller, and Heiss (1) have published approximate results on the polymerization of ω-hydroxyundecanoic acid at 200°C. Within the experimental error the course of the reaction is third order up to a degree of polymerization of 68. There is no indication of a depression in rate constant with increasing average molecular weight.

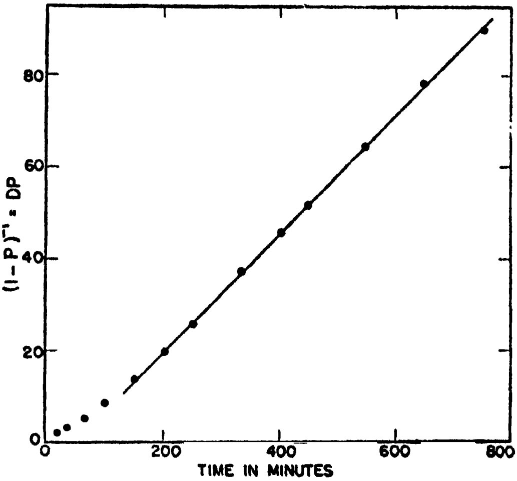


FIG. 4. Reaction of diethylene glycol with adipic acid at 109°C. catalyzed by 0.4 mole per cent of *p*-toluenesulfonic acid (from reference 28).

These uncatalyzed esterifications become exceedingly slow at high degrees of esterification, owing to the high kinetic order of the reaction. Better success in extending kinetic measurements to higher degrees of polymerization has been achieved with acid-catalyzed polyesterifications (28, 32). The rate then is proportional to the product of the hydroxyl, carboxyl, and acid catalyst concentrations

$$-dC/dt = k'C_{cat}C^2$$

where C_{cat} represents the catalyst concentration. Since the catalyst concentration is constant, the reaction is second order, and the integrated expression assumes the familiar form

$$C_0C_{cat}k't = 1/(1 - p) - \text{Const.} \tag{2}$$

In figure 4 results for the reaction of diethylene glycol with adipic acid catalyzed by *p*-toluenesulfonic acid (28) are plotted as a second-order reaction.

Over the early portion of the reaction there is curvature similar to that observed in the uncatalyzed polyesterifications. Thereafter, and at least as far as a degree of polymerization of 90, the disappearance of functional groups is accurately second order. The velocity constant therefore is not affected by molecular size up at least to a molecular weight of 10,000. Concurrently, the viscosity increased over two thousandfold. Similar results have been reported for the polymerization of decamethylene glycol with adipic acid catalyzed by *p*-toluenesulfonic acid (32).

The argument presented by Schulz (80) that the rate-controlling step in polyesterification is the removal of water, the esterification process being at or near equilibrium with the water present at advanced stages of the reaction, can be refuted in various ways. The rate constants and temperature coefficients observed in the experiments discussed above are typical of esterifications, the observed rate is accelerated immensely by catalysts, and the rate is not increased by reducing the pressure (28) to accelerate removal of water.

C. Experimental results on other condensation polymerizations

Kienle and coworkers (54) have reported carefully conducted experiments on the course of three-dimensional polyesterifications. They co-reacted glycerol with various dibasic acids: phthalic, succinic, maleic, adipic, and sebacic. In addition to the concentration of free carboxyl groups, they also measured the water evolved as a function of time. Kinetic analysis of their data is complicated by the peculiarity previously discussed of the esterification reaction up to 80 or 90 per cent conversion and by the somewhat lower reactivity of the secondary hydroxyl group of glycerol (77). The reaction progresses smoothly, following a course similar to that observed in the bifunctional polyesterifications discussed above. The data do not support the stepwise reaction mechanism proposed by Kienle. It is interesting to note that water evolution continues smoothly through the gel point, where the macroscopic viscosity reaches infinity.

Satisfactory kinetic data on condensation polymerizations other than polyesterifications are scarce. Polyamidation has been reported (33) to be second order with respect to the functional groups, in conformity with monofunctional amidation (69). Dostal and Raff (25) have investigated the mechanism of the condensation of *p*-cresol with formaldehyde. However, they determined the percentage of polymer rather than the concentration of functional groups as a function of time, and their results are of little value therefore in describing the course of the condensation process in its more important stages.

D. Conclusions

The experimental results discussed above demonstrate that the susceptibility of a functional group to chemical reaction is not affected by the size of the molecule to which it is attached, nor does it depend ordinarily on the viscosity of the reaction medium. Contrary to the contentions of various authors on the subject, this conclusion in no way contradicts the theoretical principles of reactivity and chemical kinetics. It is supported further by investigations on the rates of degradation of polymer molecules, to be discussed in the next section.

In general, therefore, condensation polymerizations can be expected to proceed in a manner paralleling exactly the analogous monofunctional reaction. In drawing this analogy, however, it is necessary to focus attention on the functional groups and not on the percentage of polymer. If, as is most often the case, the monofunctional condensation reaction is second order, then the disappearance of functional groups in the polyfunctional reaction will also be second order. If the rate of the monofunctional reaction is accelerated in proportion to the concentration of a certain catalyst, this catalyst will influence the polyfunctional reaction similarly, etc.

The functional groups of the polymerizing molecules evidently react with one another at random. This conclusion is of foremost importance to the theory of the constitution of condensation polymers, to be discussed in subsequent sections of this review.

V. KINETICS OF DEGRADATION PROCESSES

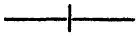
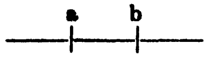
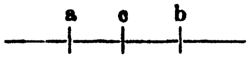
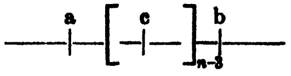
A. Cellulose and cellulose derivatives

When dissolved in strong acids cellulose is degraded through hydrolytic splitting of the β-glucoside linkages between the structural units of the cellulose chain:

$$\mathrm{HO(C_6H_{10}O_4)—[O—(C_6H_{10}O_4)]_{n-2}—O—(C_6H_{10}O_4)OH}$$

The process can be followed viscometrically, polarimetrically, or by chemical determination of the aldose end group produced for each bond split. Measurements by Freudenberg and coworkers (41, 42), employing the latter two methods and interpreted according to the theoretical treatments supplied by Kuhn (58, 59), show a continuous increase in the first-order velocity constant for the splitting of the inter-unit linkages over the range from 10 to 100 per cent hydrolysis, corresponding to a change in $\overline{DP}_n$ from 10 to 1. In other words, the linkages remaining near completion of the degradation split with greater ease, on an average, than those initially present.

They also measured rates of hydrolysis, under the same conditions, of several lower polysaccharides: namely, those for which n in the above formula equaled 2, 3, and 4, respectively. Initial concentrations were adjusted to give equal concentrations of glucose at complete hydrolysis. Whereas hydrolysis of the bond in cellobiose progressed in strict accordance with a first-order expression, the calculated first-order rate constants for the disappearance of total β-glucoside bonds for cellotriose and cellotetrose increased as the reaction progressed. Initial rate constants (in 51 per cent sulfuric acid at 18°C.) for hydrolysis of these polysaccharides, expressed as the fraction of inter-unit linkages disappearing per minute, were as follows:

POLYSACCHARIDE	SCHEMATIC STRUCTURE	INITIAL RATE CONSTANTS
		$min.^{-1} \times 10^4$
Cellobiose		1.07
Cellotriose		0.64
Cellotetrose		0.51
Cellulose		0.305

Freudenberg and Kuhn (41, 42) showed that both the velocity constants and the courses followed by the hydrolyses of these various polymers can be accounted for by postulating that one or the other or both of the terminal linkages, a and b, in these various species hydrolyzes more rapidly than internal c linkages. All of the latter can be assumed to hydrolyze at the same rate, or at least their rates are not perceptibly different. If it is assumed, for example, that one of the two terminal linkages, a or b, in an n-mer reacts at a rate equal to cellobiose, 1.07×10^{-4}, and that for each of the other $n - 2$ linkages the rate corresponds to the initial average rate, 0.305×10^{-4}, of hydrolysis of the bonds in cellulose ($n \rightarrow \infty$), then the calculated initial rates for cellotriose and cellotetrose, 0.69×10^{-4} and 0.56×10^{-4}, respectively, are in fair agreement with the observed values. Also, the course of the hydrolysis of cellulose is in good agreement with Kuhn's mathematical analysis (59) of the consecutive reaction problem precipitated by the above postulate.

These results probably can be explained equally well by assuming that the enhanced reactivity is shared jointly by both terminal linkages a and b, neither being as reactive as the linkage in cellobiose (41). Mathematical analysis of the course of the hydrolysis of cellulose in this case is considerably more difficult. However the relative reactivities of the linkages a and b may be related, the results with cellulose indicate that the reactivity of internal c linkages is about constant, independent of molecular weight over the range investigated, i.e., up to $\overline{DP}_n = 10$. The lesser reactivities of the internal linkages can reasonably be ascribed to the short-range substitution effect previously discussed.

The course of the degradation of methylated cellulose in fuming hydrochloric acid at 0°C. was observed by Wolfrom, Sowden, and Lassettre (92) by continuous mercaptalation of the aldose group formed at each bond ruptured. Sulfur analysis gave a direct measure of the number of bonds split. Over the range of their measurements, from $\overline{DP}_n = 150$ to 50, the concentration of unhydrolyzed bonds is almost constant. If the reactivity of the bonds is independent of molecular weight therefore, the number of bonds hydrolyzed should increase linearly with time over this range. That this is the case is shown by the data of Wolfrom and coworkers in figure 5. Had their measurements been extended to greater degrees of hydrolysis, enhanced reactivity of terminal linkages as observed by Freudenberg and Kuhn probably would have been in evidence.

The hydrolysis of cellulose of high molecular weight is best observed viscometrically. The change in the number of end groups over the initial portion of the degradation is too small to be measured accurately by chemical means. The polarimetric method is likewise insufficiently sensitive at high molecular weights. Schulz and Löhmann (82) followed the degradation of celluloses varying from 130 to 1500 units in length dissolved in phosphoric acid by measuring dilute solution viscosity. They originally concluded from their results that the rate of splitting of inter-unit bonds is first order and that the velocity constant is independent of molecular weight. Subsequently (81), they found that the intermediate degraded celluloses were less heterogeneous than would be true if bonds were split strictly at random. Chains of about 500 units were in much greater abundance than would be obtained by random degradation. Schulz and coworkers revised their original conclusions to the extent of postulating that at regular intervals of around 500 units, linkages occur which are much more readily hydrolyzed than the β-glucoside linkages. They suggested that these exceptional linkages are occasioned by the occurrence of xylose units at these intervals.

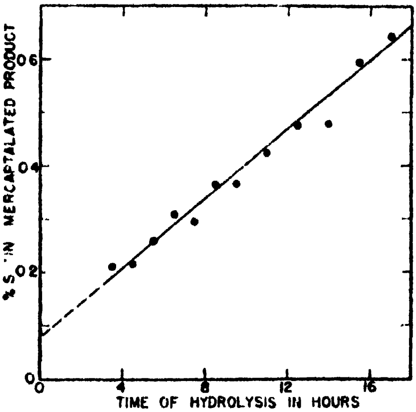


FIG. 5. Hydrolysis of methylated cellulose in fuming hydrochloric acid at 0°C. Reaction followed by mercaptalation method. (Wolfrom, Sowden, and Lassettre (92).)

From a degree of polymerization of about 500 units onward, the hydrolysis of linkages in the cellulose chain is first order. At more advanced stages of the hydrolysis the rate is somewhat more rapid than first order, but this behavior is caused by the greater abundance of more easily hydrolyzed terminal linkages, as found by Freudenberg, Kuhn, and coworkers.

From the various results discussed above it is clear that the *internal* linkages between the units of cellulose and derivatives are equivalent in their reactivity toward hydrolysis regardless of their location in the chain and independent of the length of the chain, at least up to *DP* = 500. At higher molecular weights weaker linkages may be present, owing to specific differences in the chemical character of occasional units of the chain. There is no evidence for an effect of molecular weight *per se* on reactivity up to $DP = 1500$ (molecular weight = 250,000).

B. *Hydrolysis of polyamides*

Hydrolysis of the polypeptide of glycine

$$NH_2CH_2CO—[NHCH_2CO]_{n-2}—NHCH_2COO^-$$

in alkaline solution (43, 61) follows a pattern similar to that observed for cellulose. In view of the short length of the structural unit and the ionic character of one of the end groups (in alkaline solution), terminal bonds should be expected to possess reactivities differing from internal bonds. In this case the terminal bonds are observed to be less reactive than internal ones. Freudenberg and coworkers (43) showed that the course of the hydrolysis of a synthetic polypeptide of glycine having a $\overline{DP}_n$ of 8 was accurately described by assigning a mean rate for the two terminal bonds a and b (see diagram given above for polysaccharides) equal to the observed initial rate of hydrolysis of the peptide bonds in diglycylglycine ($n = 3$) and a rate for the internal bonds equal to the rate previously deduced (61) for the hydrolysis of the c bond in triglycylglycine ($n = 4$).

Scatchard, Oncley, Williams, and Brown (78) recently presented an interesting interpretation of the hydrolytic degradation of the protein collagen to gelatin and the further degradation of gelatin. They consider that collagen consists of very long polypeptide chains having readily hydrolyzable bonds at regular intervals. In the preparation of gelatin nearly all of these are split, and in addition a small fraction of the less reactive peptide bonds of the resulting fragment (gelatin) molecules are hydrolyzed as well. It is estimated that these easily hydrolyzable bonds of collagen occur at intervals of about 1200 units. In the further degradation of these "fragments" (molecular weight *ca.* 100,000) the rate of splitting of the peptide bonds is observed to be constant for small degrees of reaction. Hence, it is inferred that all linkages in the gelatin molecules are equally susceptible to hydrolysis, and that their reactivity is independent of molecular weight. The degradation of gelatin would appear, therefore, to consist of random splitting of molecules initially uniform in molecular weight. The theoretical treatment of this type of degradation was solved previously by Montroll and Simha (68) and, in a simpler fashion, by Sakurada and Okamura (76). By comparing osmotic-pressure molecular weights of partially degraded gelatin with sedimentation-equilibrium measurements in the ultracentrifuge ("*z*-average" molecular weight), Scatchard and coworkers were able to show that the molecular-weight heterogeneity is indeed consistent with the view that degradation of gelatin proceeds by random splitting of initially uniform chains. This interpretation of the degradation of the parent collagen chains is strikingly similar to that proposed by Schulz, Husemann, and Löhmann (81) for native cellulose.

Matthes (65) measured the rate of hydrolysis in 40 per cent sulfuric acid at 50°C. of the polyamide

$$NH_3^+—(CH_2)_5CO—[NH(CH_2)_5CO]_{n-2}—NH(CH_2)_5COOH$$

derived from ε-aminocaproic acid. The degree of polymerization decreases strictly in accordance with a first-order splitting of amide linkages over the entire range investigated from $\overline{DP}_n = 220$ to 6.

C. *Alcoholysis of polyesters*

The kinetics of degradation by alcoholysis of linear polyesters prepared from decamethylene glycol and adipic acid

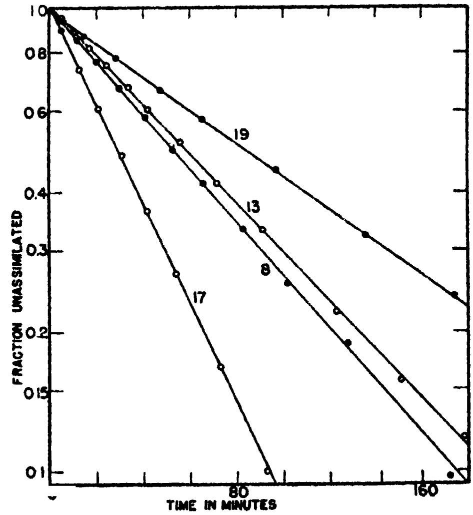
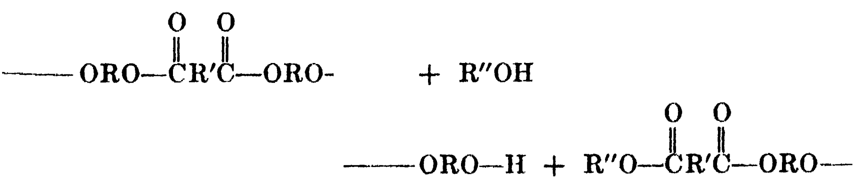


FIG. 6. The partial degradation of decamethylene adipate polyester with small percentages of decamethylene glycol (experiments 8, 13, and 17), or with lauryl alcohol (experiment 19) at 109°C. catalyzed with 0.1 equivalent per cent of *p*-toluenesulfonic acid (31). The fraction of glycol, or alcohol, unassimilated, calculated indirectly from melt viscosity measurements, is plotted on the logarithmic ordinate scale.



$$——ORO—\overset{O}{\overset{\|}{C}}R'\overset{O}{\overset{\|}{C}}—ORO- \quad + R''OH \rightarrow ——ORO—H + R''O—\overset{O}{\overset{\|}{C}}R'\overset{O}{\overset{\|}{C}}—ORO—$$

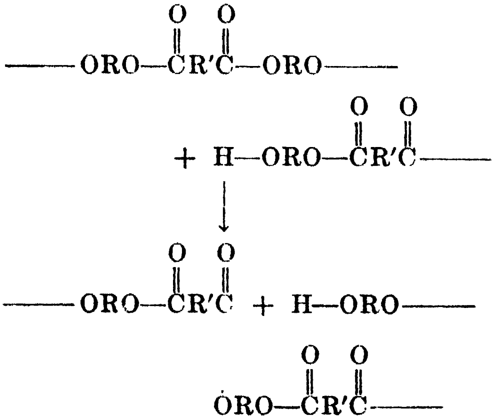
was investigated (31) by a novel method in which the degree of polymerization at various stages of the reaction was computed from the viscosity of the reaction mixture, consisting of polyester plus a small percentage of alcohol, or glycol. The exact empirical relationship (29) between melt viscosity and molecular weight is the basis for this method. Not only is the measurement of the melt viscosity extremely simple; it can be conducted within the reaction vessel without removal of samples or interruption of the reaction.

Esterification is so similar to ester interchange in rate and mechanism as to have obscured the degradation process by simultaneous polymerization had the polyesters employed in these experiments (31) been functionally capable of further esterification. To avoid this difficulty, the polyesters were prepared using a small excess of glycol and the reaction was carried very nearly to completion. The polymers so obtained contained a negligible proportion of free carboxyl groups. Hence, the possibility of further esterification during the interchange experiments was practically eliminated.

In these degradations (31), in contrast to those previously discussed, a small proportion of degrading agent (alcohol or glycol) was employed. The final product of the degradation was a polymer of lower molecular weight than the initial product, rather than the free monomers. From the viscosity at a given stage of the reaction the average molecular weight was calculated, and from this the amount of alcohol (or glycol) assimilated by the polymer through the interchange reaction could be computed. In view of the constancy of the number of ester groups the reaction should be first order with respect to the alcohol, provided, of course, that all ester groups are equally reactive. That this is the case is shown by the linear plots in figure 6 for the reaction at 109°C. catalyzed by *p*-toluenesulfonic acid. In these experiments polymers of initial $\overline{DP}_n$ = 35 to 40 were degraded to $\overline{DP}_n$'s of around 15 to 20.

D. Interchange reactions in condensation polymers

The ready occurrence of the interchange reaction between an alcohol and a polyester suggests at once that polyester molecules bearing terminal hydroxyl groups should be capable of reacting with one another, thus:



$$
\begin{aligned}
&\text{——ORO—}\overset{\overset{O}{\|}}{C}R'\overset{\overset{O}{\|}}{C}\text{—ORO——}\\
&\qquad\qquad + \text{H—ORO—}\overset{\overset{O}{\|}}{C}R'\overset{\overset{O}{\|}}{C}\text{——}\\
&\qquad\qquad\qquad\downarrow\\
&\text{——ORO—}\overset{\overset{O}{\|}}{C}R'\overset{\overset{O}{\|}}{C} + \text{H—ORO——}\\
&\qquad\qquad\text{ORO—}\overset{\overset{O}{\|}}{C}R'\overset{\overset{O}{\|}}{C}\text{——}
\end{aligned}
$$

(I)

A similar interchange may occur between a carboxy acid end group and an ester, but the rate of this reaction is known to be much slower than the alcoholysis reaction given above. In these interchange reactions between polymer molecules there is no net change in the number of inter-unit linkages, and the number of molecules on either side of the equation is the same. The number-average molecular weight is unaffected therefore. However, these processes can bring about changes in molecular-weight distribution. For example, two average molecules can react to produce one much longer and another correspondingly shorter than the average. Conversely, if a mixture is composed of two species, one very long and the other quite short, they may conceivably interchange with each other to produce polymers intermediate in size.

A fully satisfactory account of the rôle and importance of these interchange processes in condensation polymers would necessitate detailed consideration of the subject of molecular-weight distribution, to be covered in the next section. For the purposes of the present qualitative discussion it will be sufficient to point out the rather obvious fact that, regardless of the initial distribution of molecular weights at commencement of interchange, ultimately the interchange processes will lead to a state of (dynamic) equilibrium in which the concentration of each species remains constant. These concentrations define the "equilibrium molecular weight distribution" (38, 39, 90) for a given (fixed) extent of polymerization, or number of inter-unit linkages. Incidentally, this distribution happens to be identical with that which is obtained directly from random intermolecular condensation without simultaneous, or subsequent, occurrence of interchange reactions (38). Thus, interchange, though it may occur freely, ordinarily will have no effect on the molecular-weight distribution of a condensation polymer. (Important exceptions will be noted later.) The current discussion will be confined to linear polymers, but similar conclusions obviously may be applied to three-dimensional polymers as well.

For the purpose of experimentally observing the occurrence of interchange between polymer molecules, two polydecamethylene adipates, one of low and another of high average molecular weight, were mixed (38). These polymers were so prepared that their end groups were predominantly hydroxyl, in order to minimize simultaneous occurrence of esterification. *p*-Toluenesulfonic acid catalyst was used, and the mixture was fused and heated at 109°C. Ordinary chemical methods would be useless for observing the interchange, owing to the constancy of the concentrations of ester linkages and terminal hydroxyls. The melt viscosity, however, depends not on the number-average molecular weight $\overline{M}_n$, which is constant, but on the weight average $\overline{M}_w$, which shifts as the molecular-weight distribution is altered (at constant $\overline{M}_n$). The empirical relationship between melt viscosity and weight-average molecular weight (29) being known, it was possible to observe the change in distribution due to interchange by simple melt viscosity measurements on the reaction mixture.

One set of results is shown in figure 7. The viscosity dropped rapidly at first, and then approached a limiting value asymptotically. This decrease in viscosity of nearly 60 per cent was produced entirely by alteration of the molecular-weight distribution. The total number of molecules, and $\overline{M}_n$ as well, necessarily remained constant, owing to the nature of the reactants, but the numbers of the larger molecular species were drastically decreased through interchange. These larger molecules exerted a greater influence on the viscosity than the smaller ones; hence, a decrease in viscosity accompanied equilibration of the size distribution. The observed final viscosity is close to that calculated for the equilibrium distribution (38) having the number-average molecular weight dictated by the molecular weights and proportions of the initial ingredients. The agreement lies within the limits of accuracy of the empirical viscosity relationship as applied to these particular polymers.

Interchange also may occur in other condensation polymers. Brubaker, Coffman, and McGrew (4) have shown that when two polyamides formed from different monomers (e.g., one formed from triglycol diamine and adipic acid and the other from hexamethylenediamine and adipic acid) are heated together for about 30 min. at 285°C., they combine to give a product differing from both initial polymers. This product is not merely a mixture of molecules of the two original components, as is shown by their inseparability by the action of a selective solvent. The product differs, also, from the copolymer of the same composition prepared directly from the monomers.

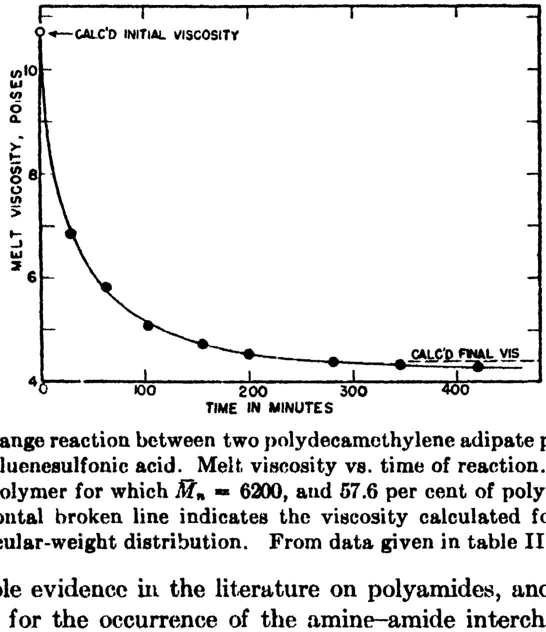
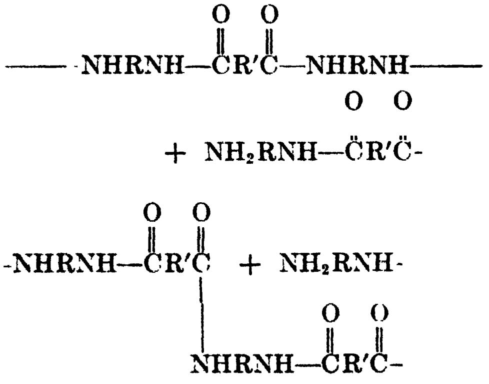


FIG. 7. Interchange reaction between two polydecamethylene adipate polymers at 109°C catalyzed by *p*-toluenesulfonic acid. Melt viscosity vs. time of reaction. Initial mixture: 42.4 per cent of polymer for which $\bar{M}_n = 6200$, and 57.6 per cent of polymer having $\bar{M}_n = 1860$. The horizontal broken line indicates the viscosity calculated for the theoretical equilibrium molecular-weight distribution. From data given in table II of reference 38.

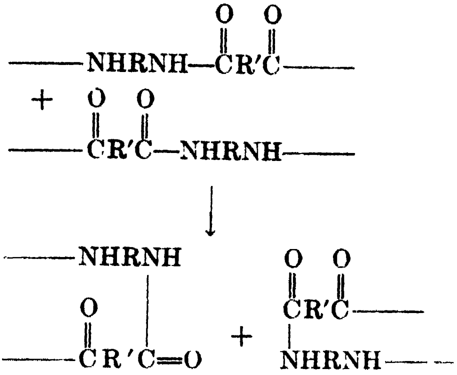
There is ample evidence in the literature on polyamides, and on monomeric amides as well, for the occurrence of the amine–amide interchange reaction



$$\text{——NHRNH—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{R}'\overset{\text{O}}{\overset{\|}{\text{C}}}\text{—NHRNH——} + \text{NH}_2\text{RNH—}\overset{\text{O}}{\ddot{\text{C}}}\text{R}'\overset{\text{O}}{\ddot{\text{C}}}\text{-}$$

$$\text{-NHRNH—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{R}'\underset{\text{NHRNH—}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{R}'\overset{\text{O}}{\overset{\|}{\text{C}}}\text{-}}{\underset{|}{\overset{\text{O}}{\overset{\|}{\text{C}}}}} + \text{NH}_2\text{RNH-} \qquad \text{(II)}$$

which is analogous to the polyester interchange (I) given above. It is likely, furthermore, that another type of interchange—namely, interchange between two amide linkages—can occur in polyamides:



$$\begin{array}{l}\text{———NHRNH—}\overset{\overset{\displaystyle O}{\|}}{C}R'\overset{\overset{\displaystyle O}{\|}}{C}\text{———}\\ +\\ \text{———}\overset{\overset{\displaystyle O}{\|}}{C}R'\overset{\overset{\displaystyle O}{\|}}{C}\text{—NHRNH———}\end{array} \Big\downarrow \begin{array}{l}\text{———NHRNH}\\ \qquad\qquad | \\ \text{———}\overset{\overset{\displaystyle O}{\|}}{C}R'C{=}O\end{array} + \begin{array}{l}\overset{\overset{\displaystyle O}{\|}}{C}R'\overset{\overset{\displaystyle O}{\|}}{C}\text{———}\\ | \\ \text{NHRNH———}\end{array}$$

(III)

In the experiments reported by Brubaker *et al.*, evidently interchange occurred by way of either, or both, of these processes (II and III) to the extent that few of the initial polymer molecules remained intact. The reaction was not, however, allowed to continue until interchange reactions had brought about the state of equilibrium in which the units would be combined purely at random, as in copolymers prepared directly from the same monomers.

The counterpart of reaction III in polyesters, i.e., ester–ester interchange, proceeds at an extremely slow rate, if indeed it occurs at all. Little is known concerning interchange reactions in other polymers, aside from what can be inferred from the known chemical characteristics of the linkage. As has already been mentioned, ring–chain interconversions undoubtedly proceed by interchange reactions. Hence, the occurrence of this interconversion in a given case would indicate that interchange between polymers can also occur, although the rates may differ considerably (particularly if the ring is one of six members). Polyanhydrides certainly interchange readily with carboxylic acid end groups, in analogy with I and II above. Whether or not anhydride–anhydride interchange, like III, occurs is not known, but the acceleration of the conversion of cyclic anhydrides to linear polymers by traces of water favors the former mechanism.

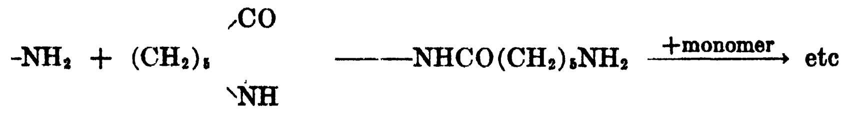
In some cases the linkage is too stable to enter readily into interchange reactions, e.g., in the hydrocarbon polymers prepared from decamethylene dibromide and sodium, in polyethylene oxide

$$HO\text{—}[CH_2CH_2O]_{x-1}\text{—}CH_2CH_2OH$$

(although classification of this as a condensation polymer is questionable), to a considerable degree in polymeric sulfides, and in cellulose and its derivatives.

The concept of mobile reshuffling of sections of high-polymer molecules, and the consequent transitory existence of individual molecules, at temperatures far below their decomposition points is interesting in itself. As pointed out above, the process is of importance in altering the distribution of an artificial mixture of two polymers from the same monomers but differing in average molecular weight, and in cross-blending the molecules of two polymers prepared from different monomers and subsequently heated together. It should also be mentioned that Carothers (6, 12) employed polymer interchange in producing high-molecular-weight polyesters from a substantial stoichiometric excess of ethylene glycol over dibasic acid. The initial products were of low molecular weight, owing to the excess of glycol, but on further heating in vacuum excess glycol was removed and the molecular weight was advanced. Now the amount of free glycol remaining at completion of the esterification of 5 mole per cent excess of glycol over dibasic acid (without loss of glycol) is extremely small—about 0.25 per cent of the initial amount of glycol. However, as this is removed by vaporization, interchange between hydroxyl terminal groups and, in this case, the ester linkages nearest the ends of chains will tend to restore the equilibrium concentration of free glycol. Hence, more glycol can be removed and the average degree of polymerization advances gradually.

Interchange may be of importance (38) also in altering the distribution of molecular weights in polymers prepared from cyclic compounds. In the case of ϵ-caprolactam, for example, if polymerization is brought about by relatively few free amino groups, possibly belonging to ϵ-aminocaproic acid molecules introduced at the start, and the reaction proceeds according to the following mechanism:



$$\text{-}NH_2 + (CH_2)_5\begin{matrix}\nearrow CO\\ \\ \searrow NH\end{matrix} \quad \text{———}NHCO(CH_2)_5NH_2 \xrightarrow{+\text{monomer}} \text{etc}$$

then the final molecular-weight distribution will be unusually sharp (30) (Poisson distribution); its homogeneity with respect to molecular size will be better than is attainable by a very careful fractionation of a polymer of the usual degree of heterogeneity. This is a direct consequence of the above mechanism: successive addition of monomers to a fixed number of equivalent terminal groups (30). If the reaction conditions are such that interchange reactions also occur, and in the above example this is likely to be the case, the molecular-weight distribution will shift to the much broader equilibrium distribution (see figure 9).

VI. CONSTITUTION OF LINEAR CONDENSATION POLYMERS

A. Molecular weights of linear polymers

In a straightforward condensation of bifunctional units of the hydroxy acid or amino acid type, which for the sake of generality can be represented as

$$A\text{—}B \rightarrow A\text{—}BA\text{—}BA\text{—}\text{etc.} \qquad \text{(type i)}$$

where A and B are the complementary functional groups and AB is the linkage formed by their condensation with one another, the number of molecules necessarily will equal the number of unreacted A or B groups. The average molecular weight (number average), $\bar{M}_n$, will be given by the reciprocal of the number of moles of unreacted A or B groups per gram. The same will be true of a glycol–dibasic acid condensation

$$\text{A—A} + \text{B—B} \rightarrow \text{A—AB—BA—etc.} \qquad \text{(type ii)}$$

provided that precisely equivalent quantities of the two reactants are employed and that no loss of either reactant occurs by volatilization. The condensations are assumed to occur without interference from side reactions. The degree of polymerization, $\overline{DP}_n$, for either type will be given by the quotient of the total number of units, N_0, divided by the total number of molecules. The latter, being equal to the number of unreacted A or B groups, is given by $N_0(1 - p)$, where p is the extent of reaction previously employed. Hence, for linear polymerization of bifunctional units (exclusively) in which equimolar quantities of A and B groups are present:

$$\overline{DP}_n = 1/(1 - p) \qquad (3)$$

At 95 per cent reaction ($p = 0.95$) there will be an average of twenty units per molecule; at 99 per cent reaction, one hundred units; etc. The problem of attaining high molecular weight reduces to the problem of forcing the condensation reaction as nearly as possible to completion. At the same time, side reactions which otherwise consume functional groups must be reduced to a very low minimum (29).

If the reaction is second order, then according to equation 2:

$$\overline{DP}_n = \text{Const.} \times t + 1 \qquad (4)$$

In accordance with this relationship, the average molecular weight in acid-catalyzed polyesterifications increases linearly with time (figure 4).

If the reaction is third order, then according to equation 1:

$$\overline{DP}_n = (\text{Const.} \times t + 1)^{1/2} \qquad (5)$$

Except at very low $\overline{DP}_n$'s

$$\overline{DP}_n = \text{Const.} \times t^{1/2} \qquad (5')$$

Thus, in third-order polyesterifications (uncatalyzed) and in uncatalyzed polyanilidation (33), high molecular weights are reached only by continuing the reaction for a long time. This is not the result of inherent sluggishness of the reaction owing to high viscosity, nor is it due to the difficulty with which water formed in the reaction is removed from the polymer, as was once supposed (14). The third-order reaction between functional groups permits the average molecular weight to increase only in proportion to the square root of the time; hence the apparent falling off in the rate of polymerization as the molecular weight increases (28).

Molecular weights of linear condensation polymers can be controlled by discontinuing the reaction at the desired stage. However, the polymers produced in this way may undergo further condensation if heated subsequently, as, for example, in the course of processing and fabricating operations. The resultant change in properties frequently is undesirable.

This susceptibility to further polymerization can be avoided and the molecular weight can be controlled by the application of the "molecular weight stabilization" method for controlling molecular weight (12, 72). This is accomplished by displacing the precise stoichiometric balance between the primary bifunctional reactants through the addition of a small amount of a so-called "molecular weight stabilizer", which is nothing more than a monofunctional or bifunctional reactant incorporated in small proportion with the primary monomers.

For example, lauric acid has been used in the stabilization of polyamides (72). If the reactant is an amino acid, at completion of the reaction the lauric acid-stabilized molecules will have the structure

$$\mathrm{RCO{-}[NHR'CO]_{x-2}{-}NHR'COOH}$$

If lauric acid is added to a stoichiometric mixture of a dibasic acid and a diamine, the molecules produced at complete amidation will be of three types:

$$\mathrm{RCO{-}[NHR'NHCOR''CO]_{(x-1)/2}{-}OH}$$

$$\mathrm{RCO{-}[NHR'NHCOR''CO]_{(x-3)/2}{-}NHR'NH{-}COR}$$

$$\mathrm{HOCOR''CO{-}[NHR'NHCOR''CO]_{(x-1)/2}{-}OH}$$

Similarly, an excess of one or the other reactant in a type ii linear condensation may perform the function of a molecular-weight stabilizer. For example, an excess of dibasic acid in a glycol–dibasic acid condensation causes the product of complete esterification to have the formula

$$\mathrm{HOCOR'CO{-}[OROCOR'CO]_{(x-1)/2}{-}OH}$$

The relationship of the molecular weight, or degree of polymerization, to the proportion of stabilizer employed and the extent of completion of the condensation can be computed in various ways. One which is quite general (27, 29) is given here. Consider a condensation either of type i or of type ii, in which first of all the reactants are present in stoichiometric quantities. To either of these is added a stabilizer B—B, which may or may not be identical with one of the co-reactants in the type ii reaction. Let

N_A = total number of A groups initially present
N_B = total number of B groups initially present
$r = N_A/N_B$
p = fraction of A groups which have reacted at a given stage of the reaction.

The total number of units is given by

$$(N_A + N_B)/2 = N_A(1 + 1/r)/2$$

The total number of ends of chains can be expressed as

$$2N_A(1 - p) + (N_B - N_A) = N_A[2(1 - p) + (1 - r)/r]$$

and this must equal twice the total number of molecules, since each linear molecule has two ends. The number-average degree of polymerization is given by

$$\overline{DP}_n = \frac{\text{Number of units}}{\text{Number of molecules}} = \frac{1 + r}{2r(1 - p) + 1 - r} \qquad (6)$$

At completion of the reaction ($p = 1$)

$$\overline{DP}_n = (1 + r)/(1 - r) \qquad (7)$$

$$= \frac{\begin{pmatrix}\text{Moles bifunctional units}\\ \text{exclusive of stabilizer}\end{pmatrix}}{(\text{Moles stabilizer units})} + 1 \qquad (7')$$

The same equations are applicable to stabilization with monofunctional units B—, provided that r is redefined as follows:

$$r = N_A/(N_A + 2N_{B-})$$

Equation 7′ requires no revision. Other special cases can be similarly treated, as, for example, when two or more types of stabilizers are employed simultaneously.

Equations 7 and 7′ emphasize the marked effect of a small amount of stabilizer in limiting the ultimately attainable molecular weight. One mole per cent of stabilizer units limits the average degree of polymerization to about one hundred units, for example. It emphasizes further the precision with which the stoichiometric balance must be maintained in linear condensation in order for high molecular weights to be reached. Loss of a fraction of a per cent of one or the other ingredient in a type ii condensation through volatilization from the reaction mixture, or loss of functional groups through side reactions in either type of condensation, may appreciably limit the molecular weight attainable.

The effects of loss of ingredient, of side reactions, and of monofunctional impurities in vitiating molecular weights derived from chemical determination of one or the other end group have been discussed previously (29) in some detail. This source of error, though small at low degrees of polymerization, increases approximately as the square of $\overline{DP}_n$. The percentage error increases directly with the molecular weight and to a close approximation is given by

$$(\text{Per cent excess of one unit}) \times \overline{DP}_n/2$$

Thus, at $\overline{DP}_n = 200$, a loss of 0.1 per cent of one or the other of the bifunctional reactants A—A or B—B introduces a 10 per cent error in the value of the molecular weight calculated directly from the number of terminal A or B groups.

Molecular weights of synthetic condensation polymers almost invariably have been determined by end-group methods. The viscosity methods (solution or melt) which may be employed have been established on the basis of end-group determinations. Cryoscopic and ebullioscopic methods may be sufficiently accurate below about 5000 molecular weight, and in this region agreement with end-group methods has been confirmed (12, 85). Kraemer and Van Natta (57) reported an ultracentrifuge sedimentation value for a polyhydroxydecanoic acid of about 25,000 molecular weight which was in good agreement with the end-group titration value (19). However, this agreement is of dubious significance in view of the ambiguity in the type of average obtained from the ultracentrifuge data, as well as the probability of sufficient pyrolytic loss of functional groups at the high temperature used in synthesis (40) to vitiate the end-group molecular weight.

B. Molecular-weight distribution in linear condensation polymers

The principle of equal reactivity of all functional groups during condensation polymerization is the foundation for the theoretical derivation of molecular size distribution relationships (27). No other postulates or assumptions are required. At every stage of the polymerization equal opportunities for reaction are available to all unreacted functional groups. At conclusion of the condensation the probability that a given functional group has reacted (when $r = 1$) is invariably equal to p, the fraction of all functional groups which have reacted. The significance of this statement lies in the fact that if a given unit is known to be attached through one reacted functional group to a sequence of n consecutive units, the probability that the other functional group of the unit has reacted is still equal to p, and independent of the length of the chain as indicated by n.

Consider, for example, the polyester produced from an ω-hydroxy acid. Suppose that a terminal hydroxyl group of one of the molecules has been located at random and we wish to know the probability that this molecule is composed of exactly x units.

$$\underset{1}{\text{H—ORCO}}\text{—}\underset{2}{\text{ORCO}}\text{—}\cdots\cdots\text{—}\underset{x-1}{\text{ORCO}}\text{—}\underset{x}{\text{OH}}$$

The probability that the carboxyl group of the first unit is esterified is equal to p. The probability that the carboxyl of the second unit is esterified, this probability being independent of whether or not linkage 1 has been formed, is likewise equal to p. The probability that this sequence continues for $x - 1$ linkages is the product of these separate probabilities, or p^{x-1}. This is the probability that the molecule contains at least $x - 1$ ester groups, or at least x units. The probability that the x^{th} carboxyl group is unreacted, thus limiting the chain to exactly x units, is $1 - p$. Hence, the probability that the molecule in question is composed of exactly x units is given (27) by

$$P_x = p^{x-1}(1 - p) \tag{8}$$

Obviously, the probability, P_x, that any molecule selected at random is composed of x units must equal the mole fraction of x-mers.

The total number of x-mers is given by

$$N_x = N(1 - p)p^{x-1}$$

where N is the total number of molecules of all sizes. Letting N_0 represent the total number of units

$$N = N_0(1 - p)$$
$$N_x = N_0(1 - p)^2p^{x-1} \tag{9}$$

If the added weight of the end groups (equal to H + OH for each molecule) is neglected, the molecular weight of each species is directly proportional to x. Hence the weight fraction can be written

$$w_x = xN_x/N_0$$

The error introduced by this approximation will be significant only at very low molecular weights. Substituting from equation 9:

$$w_x = x(1 - p)^2p^{x-1} \tag{10}$$

The same derivation holds for type ii polymers from equivalents of A—A and B—B reactants. It also applies to polymers stabilized with small amounts of monofunctional units, although here it becomes necessary to replace the extent of reaction p with another quantity, the probability that a given functional group has reacted with a *bifunctional* monomer. Type ii polymers stabilized with an excess of one or the other ingredient will be discussed later.

If interchange reactions occur subsequent to the formation of the inter-unit linkages, the above distribution will not be altered. The basis for this statement can be indicated briefly as follows: (For more rigorous treatments of this problem see references 38, 39, and 90.) If interchange reactions occur freely, ultimately a state of dynamic equilibrium will be attained in which each species is formed at a rate equal to its destruction. The concentrations of the various species (i.e., the size distribution) will then be constant. The above size-distribution relationships were derived from the principle of equal reactivity in the *kinetic* sense that all unreacted functional groups are equally susceptible to condensation. Here it is necessary to postulate equal reactivity in the *thermodynamic* sense that all functional groups share an equal probability of existing at any instant in the reacted condition, regardless of the sizes of the molecules involved. This probability again can be designated by p, the fraction of all groups which are reacted, and the previous derivations and results apply without alteration. Hence the same size distribution is obtained by interchange equilibration as is produced initially by random condensation. Polymers produced by random condensation will not be altered by interchange processes; regardless of whether the linkages are irreversibly or reversibly formed, the same molecular-weight distribution will prevail. The same distribution also is obtained by random degradation of infinitely long molecules (58).

Mole-fraction (or number) distribution curves calculated from equation 8 are shown in figure 8 for polymers having average $\bar{DP}_n$'s of 20, 50, and 100, respectively. The corresponding weight-fraction distributions calculated from equation 10 are shown in figure 9. As is also evident from the equations, monomers are present in greater numbers than any other single species, and this is true at all stages of the condensation. The number curves exhibit monotonic decreases as the number of units is increased. On a weight basis, however, the proportion of very low polymers is small, and is diminished as the average molecular weight is increased. Maxima in the weight-distribution curves occur very near the number-average value of x, i.e., very near $x = \overline{DP}_n$.

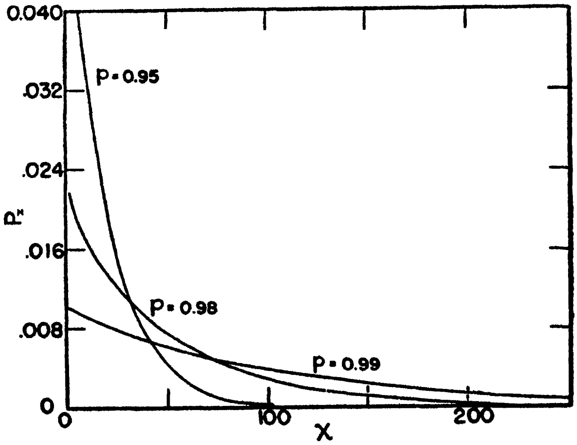


FIG. 8. Molecular-weight distributions for linear condensation polymers on a number or molar, basis for several extents of reaction p. Mole fractions P_x vs. number of structural units x, as calculated from equation 8. See reference 27.

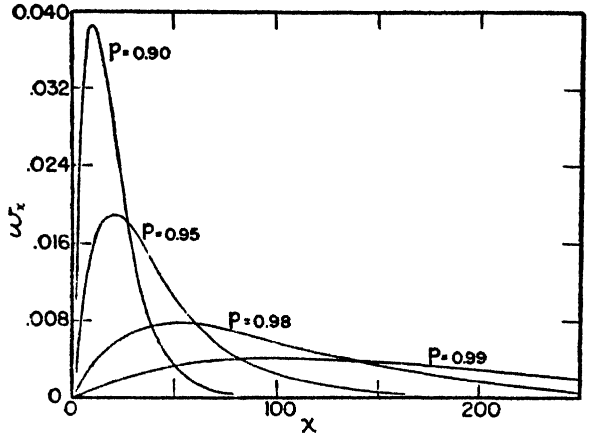


FIG. 9. Molecular-weight distributions for linear condensation polymers on a weight basis for several values of the extent of reaction p. Weight fractions w_x vs. number of structural units, x, as calculated from equation 10. See reference 27.

In type ii condensations three types of molecular species are present (27):

$$(\mathrm{A{-}AB{-}B})_{x/2} \qquad\qquad (\mathrm{A{-}AB{-}B})_{(x-1)/2}\mathrm{A{-}A}$$

Type iiAB Type iiAA

and

$$\mathrm{B{-}B(A{-}AB{-}B)}_{(x-1)/2}$$

Type iiBB

All molecules containing an even number of units necessarily will be of type iiAB, while those containing an odd number of units will be of type iiAA or iiBB. If the numbers of A—A and B—B units in the reaction mixture are exactly equal, there will be as many *even* as *odd* molecules, and the odd molecules will be equally divided between types iiAA and iiBB. The molecular-weight distribution given above applies here also; only this alternation in end groups will occur between successive even and odd values of x.

If an excess of one component is employed in the reaction, the relative numbers of these three types of species will be altered. Taking the B—B unit to be the one present in excess, there will be more type iiBB than type iiAA molecules. Furthermore, there will be more of these *odd* x molecules (including both sub-types together) than *even* molecules. This is readily evident from the fact that there are more B than A end groups. At completion of the reaction only type iiBB molecules will remain.

Mathematical expression of the distribution of sizes for these three types is rather complex (see reference 27). If the distribution for a type ii polymer containing an excess of one reactant is plotted graphically, all three types being included on a single curve, an alternation will be observed in the weight, or number, fraction from one x value to the next; there is less x-mer, where x is an even integer, than of $(x - 1)$-mer or of $(x + 1)$-mer. However, the separately considered distributions for each of the three types of molecules are virtually identical in character with the curves shown in figures 8 and 9. If an "average" distribution curve is drawn from which the alternation in abundance from one species to the next is smoothed out, the curve so obtained is virtually identical with the curve for the linear polymer formed from equal numbers of the two reactants. In conclusion, all of these variously modified bifunctional condensations yield closely similar molecular-weight distributions.

In addition to the ordinary number-average molecular weight obtained by chemical end-group methods, or by the classical thermodynamic methods (freezing-point lowering, boiling-point elevation, or osmotic pressure) for molecular-weight determination, various other average molecular weights frequently are required for the interpretation of polymer properties. The melt viscosity, for example, depends directly on the *weight-average* molecular weight (28) rather than on the *number average*. Solution viscosities usually depend on an intermediate type of average.

The number average is given by

$$\bar{M}_n = \Sigma M_x N_x / \Sigma N_x \tag{11}$$

where M_x is the molecular weight of an x-mer, and the summations are over all species from $x = 1$ to infinity. The weight-average molecular weight is defined (56) as

$$\bar{M}_w = \Sigma \bar{M}_x w_x / \Sigma w_x \tag{12}$$

Setting $M_x = xM_0$, where M_0 is the molecular weight of a structural unit, or the mean of the molecular weights of the structural units in a type ii polymer, and substituting from equations 9 and 10:

$$\bar{M}_n = M_0\Sigma[xp^{x-1}(1 - p)^2]/\Sigma[p^{x-1}(1 - p)^2]$$

The summations in this equation are equal, respectively, to 1 and to $(1 - p)$. Hence

$$\bar{M}_n = M_0/(1 - p)$$

which is the result previously obtained as expressed in equation 3. The weight average becomes

$$\bar{M}_w = M_0\Sigma[x^2p^{x-1}(1 - p)^2]/\Sigma[xp^{x-1}(1 - p)^2]$$

which reduces to

$$\bar{M}_w = M_0(1 + p)/(1 - p) \tag{13}$$

In a similar manner the root-mean-square molecular weight can be shown to be

$$\bar{M}_{rms} = M_0(1 + p)^{1/2}/(1 - p) \tag{14}$$

These various averages, or modes of the distribution, stand in the ratio (29):

$$\bar{M}_n:\bar{M}_{rms}:\bar{M}_w::1:(1 + p)^{1/2}:(1 + p)$$

When the molecular weight is large, p can be replaced by unity, and the above ratio becomes approximately $1:\sqrt{2}:2$, i.e., the various averages or modes of the distribution stand in the same ratio to one another independent of the degree of polymerization.

Direct experimental verification of the theoretical size distribution in linear condensation polymers, as expressed by equations 8 and 10, has not been reported. Determination of the molecular-weight distribution by fractionation of the polymer, followed by construction of the distribution curve from the molecular weights of the fractions, would be of little value on account of the crudity of separation which can be achieved by any known methods. Ultracentrifuge measurements have not proved satisfactory for this purpose. The recent light-scattering method for molecular-weight determination established by Debye (20, 21) is, in principle at least, applicable to this problem, but the molecular weights of condensation polymers are rather too low for best results from this method.

On the other hand, the size-distribution theory receives strong confirmation from the success with which it has been applied to various problems, including the melt viscosities of mixtures of linear polymers (29), the viscometric measurement of the rates of alcoholysis of polyesters (31), and the equilibration between low- and high-molecular-weight polyesters (38). The theory has been applied successfully to the quantitative treatment of each of these problems. If the actual distribution curve deviates appreciably from the theoretical, it must certainly be assumed that this departure will vary with the average degree of polymerization, the deviation presumably becoming greater the greater the degree of polymerization. Even a slight deviation of this character would have vitiated the agreement obtained between theory and experiment in the investigations referred to.

Logically, there is no necessity for experimental verification of the theoretical size-distribution functions. They are derived solely from the principle of equal reactivity of all functional groups, which is abundantly confirmed by experiment, not to mention the support which it receives from the theory of reactivity of large molecules. Although most of the experimental results have been obtained on polyesters, there is no reason to doubt that the equations also describe accurately the size distributions in other linear condensation polymers.

VII. CONSTITUTION OF THREE-DIMENSIONAL CONDENSATION POLYMERS

Analysis of the constitution and molecular-weight distribution of three-dimensional condensation polymers is much more difficult, as would be expected from their structures as compared with linear polymers (see table 1). Likewise, polymerization of multifunctional reactants is complicated experimentally by the occurrence of gelation, as previously discussed early in this review. The sudden transformation of the reaction mixture from a viscous liquid to an elastic material of infinite viscosity, which transformation characterizes the gel point, has been attributed to the formation of infinite network structures, i.e., molecular structures which assume macroscopic size and which extend throughout the medium. The suddenness with which gelation occurs is significant. Immediately following the gel point a small fraction of the material is insoluble in all solvents which do not react chemically in such a way as to degrade the polymer; the remainder is soluble and can be extracted from the former. Thus, two portions of the polymer can be differentiated: the soluble "sol" and the insoluble "gel", which constitutes the infinite network structures. As condensation polymerization proceeds beyond the gel point, the percentage of gel increases at the expense of sol. Simultaneously, the polymer becomes more tough and less extensible.

Another feature of three-dimensional polymerization which deserves mention is the low "molecular weight", or more accurately the low number-average molecular weight, of the polymerizing mixture at the gel point. This has been shown most clearly by Kienle and coworkers (54) in the case of glycerol–dibasic acid condensations. However, their conclusions from these observations that infinite networks are not formed at gelation, and consequently that gelation is the result of other causes, arise from a misinterpretation of the average molecular weight (34) (*cf. seq.*).

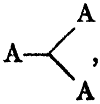
These characteristics of three-dimensional polymerizations can be shown to be necessary consequences of the polyfunctional nature of the reactants. The theory goes even further in providing quantitative relationships governing the location of the gel point, the transformation of sol to gel, and in depicting the molecular-weight distribution The method again is a statistical one. The following assumptions are employed.

All functional groups are assumed to be equally reactive, independent of the degree of polymerization and viscosity. This assumption is amply verified in the case of linear condensations, as previously discussed. Some qualification is required, however, in the case of certain multifunctional reactants such as glycerol. Here the middle (secondary) hydroxyl group is less reactive (77) than the two primary hydroxyl groups. This circumstance complicates application of the theory. If the relative reactivities of primary and secondary hydroxyl groups are known, the theory can be applied by merely employing different extent of reaction values, p' and p'', for them. In principle, then, this is no obstacle to prevent application of the statistical treatment to glycerol–dibasic (or polybasic) acid condensations. A more serious distortion could result from the possible effect of esterification of one hydroxyl on the reactivities of its neighbors, owing to their close proximity in the glycerol molecule. As already pointed out for linear polymers, this effect is likely to modify only the very low degree of polymerization portion of the molecular-weight distribution.

Condensation reactions are assumed to occur only between functional groups on different molecules, except in the case of infinite networks. This assumption that condensations involving finite species are exclusively intermolecular is the most serious source of error. The work of Kienle and coworkers (54) shows that in glycerol–dibasic acid condensations the decrease in number of molecules is perceptibly less than the number of inter-unit linkages formed. (If the reactions were exclusively intermolecular, the formation of each linkage would combine two molecules into one.) Consequently, a small part of the reaction must occur intramolecularly. This same assumption, or approximation, is inherent in the treatment of linear polymers. However, there the opportunities for intramolecular reactions were relatively much smaller.

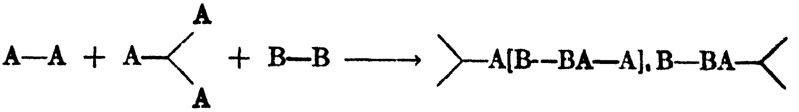
In this section the location of the gel point, the molecular-weight distribution, and the nature of the sol-to-gel conversion in three-dimensional polymers will be discussed.

A. The gel point: criteria for incipient formation of infinite networks

Consider, for example, the polymerization of a bifunctional unit A—A, a trifunctional unit  $\text{A}{-}\!\!<^{\text{A}}_{\text{A}}$, and a bifunctional unit of opposite character B—B. Structures such as that shown in figure 10 will be formed. It is the purpose of the following treatment to determine the conditions which will make possible the existence of an infinitely large, branched structure (34). In order to simplify the problem, any given molecule such as the one represented in figure 10 can be regarded as an assembly of chains connected together through trifunctional units. Each portion of a molecule between two branch units (in this case trifunctional units), or between a branch unit and a terminal unreacted functional group (e.g., OH or COOH), will be called a chain. The lengths of the chains will vary, but for the present this variation is unimportant.

First of all it is necessary to determine the branching coefficient α, which is defined as the probability that a given functional group of a branch unit leads *via* a chain of bifunctional units to another branch unit. In a polymer of the type shown in figure 10, α is the probability that an A group selected at random from one of the trifunctional units is connected to a chain the far end of which connects to another trifunctional unit. As will be shown later, both the location of the gel point and the course of the conversion of sol to gel are directly related to α.

The formation of chains, as defined above, from the reactants can be represented by the equation



where i may have any value from 0 to ∞. Other chains will be formed, one end, or both ends, of which consist of unreacted terminal groups. Under the assumption of equal reactivities of all A and of all B functional groups, the probability that the first A group on the left has reacted is given by p_A, the fraction of all A groups which have reacted; similarly, the probability that the B group on the right of the first B—B unit has reacted is given by p_B. Let ρ represent the ratio of A's (reacted and unreacted) belonging to branch units to the total number of A's in the mixture. Then, the probability that a B group has reacted with a branch unit is $p_B\rho$; the probability that it is connected to a bifunctional A—A unit is $p_B(1 - \rho)$. The probability that the A group of a branch unit is connected to the sequence of units shown in the above formula is given by

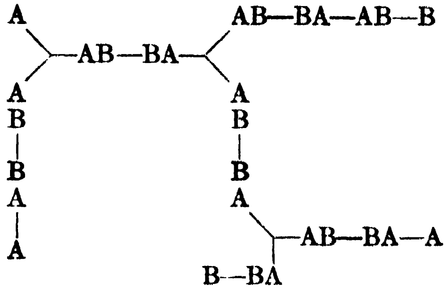
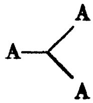


FIG. 10. Trifunctionally branched polymer composed of A—A and B—B bifunctional units, and of  trifunctional units. AB or BA is the product of the condensation of two functional groups.

$$p_A[p_B(1 - \rho)p_A]^i p_B\rho$$

The probability, α, that the chain ends in a branch unit regardless of the number, i, of bifunctional units is given by the sum of such expressions having $i = 0$, 1, 2 . . . etc., respectively. That is,

$$\alpha = \sum_{i=0}^{\infty} [p_A p_B(1 - \rho)]^i p_A p_B \rho$$

Upon evaluating this summation:

$$\alpha = p_A p_B \rho/[1 - p_A p_B(1 - \rho)] \tag{15}$$

Letting the ratio of A to B groups initially present be represented by r, as in the case of type ii linear polymers:

$$p_B = r p_A$$

Substituting in equation 15 to eliminate either p_B or p_A:

$$\alpha = r p_A^2 \rho/[1 - r p_A^2(1 - \rho] \tag{15'}$$

or

$$\alpha = p_B^2 \rho/[r - p_B^2(1 - \rho)] \tag{15''}$$

In the application of these equations, ordinarily r and ρ will be determined by the proportions of the initial ingredients employed, and either the unreacted A or B group will be determined analytically at various stages of the reaction. α can then be calculated employing either equation 15′ or equation 15″, depending on which group is determined directly. Hence, α is readily calculable from experimentally observed and controlled quantities.

Several special cases are of interest. When there are no A—A units, $\rho = 1$ and

$$\alpha = r p_A^2 = p_B^2/r \tag{16}$$

when A and B groups are present in equivalent quantities, $r = 1$, $p_A = p_B = p$, and

$$\alpha = p^2 \rho/[1 - p^2(1 - \rho)] \tag{17}$$

If the branch unit is other than trifunctional, e.g., if it is tetrafunctional, the same equations for the calculation of α can be employed; r and ρ have been so defined as to preserve these equations independent of the functionality of the branching unit. The above scheme is not completely general, however. For example, two multifunctional units, one bearing A and the other B groups, may be present. Or, a multifunctional unit bearing both A and B groups may occur. Other variations could be added. In general, an α can be calculated from the proportions of reactants and the extent of reaction by a procedure resembling that given above (34), but adapted to the particular type of reaction involved. A somewhat more difficult case is encountered when functional groups of differing reactivities are present, as in the glycerol–dibasic acid condensations already mentioned. But even here the calculation of α is feasible (34), if the necessary experimental measurements are provided.

The critical value of α at which the formation of infinite network becomes possible can be deduced as follows: If the branching unit is trifunctional, as in figure 10, each chain which terminates in a branch unit is succeeded by two more chains. If both of these terminate in branch units, four more chains are reproduced, etc. If $\alpha < 1/2$, there is less than an even chance that each chain will lead to a branch unit and thus to two more chains; there is a greater than even chance that it will end at an unreacted functional group. Under these circumstances the network cannot possibly continue indefinitely. Eventually termination of chains must outweigh continuation of the network through branching. Consequently, when $\alpha < 1/2$ all molecular structures must be limited, i.e., finite, in size.

When $\alpha > 1/2$, each chain has better than an even chance of reproducing two new chains. Two such chains will on the average reproduce 4α new chains, etc.; n chains can be expected to lead to $2n\alpha$ new chains, which is greater than n when $\alpha > 1/2$. The expected number of chains in each succeeding generation of chains is greater than the number of chains in the preceding generation. Under these circumstances, branching of successive chains *may* continue the network indefinitely. Indefinitely large structures, or what we have called infinite networks, are then possible. Hence, $\alpha = 1/2$ represents the critical condition for the incipient formation of infinite networks.

It is important to note, however, that beyond $\alpha = 1/2$ by no means all of the material will be combined into infinite molecules. For example, in spite of the favorable probability of branching, a chain selected at random may be terminated at both ends by unreacted functional groups. Or, it may possess a branch at only one end, and both of the succeeding two chains may lead to unreacted "dead ends". These and other finite species will co-exist with infinite networks so long as $1/2 < \alpha < 1$. The relative amounts of sol and gel portions will be discussed later.

The above treatment can be generalized to include polymerizations in which the branched unit is of higher functionality than three, or in which more than one type of branched unit is present. A general statement of the critical condition for formation of infinite networks is the following: Infinite network formation becomes possible when the expected number of chains (or elements) which will succeed n chains (or elements), through branching of some of them, exceeds n (34). That is, if f is the functionality of the branching units (i.e., units having a functionality greater than two), gelation will occur when $\alpha(f - 1)$ exceeds unity. The critical value of α is, therefore,

$$\alpha_c = 1/(f - 1) \tag{18}$$

If more than one type of branching unit is present, $(f - 1)$ must be replaced by the appropriate average, weighted according to the numbers of functional groups attached to the various branched units. The critical condition can be expressed in various ways, but the above is a convenient form for application to condensation polymers.

A close analogy exists between these three-dimensional polymerizations and gas-phase chain reactions which may undergo branching. If the probability of termination of the kinetic chain $(1 - \alpha)$ in the gas-phase reaction exceeds the probability of branching (α) with reproduction of two chain carriers, the chains are of finite length, and the rate of reaction attains a finite steady-state value. If the probability of branching exceeds the probability of termination, the reaction accelerates without limit and an explosion is observed. The formation of infinite networks, which as will be shown is concomitant with gelation, is analogous to explosion in chain reactions. A very slight alteration of temperature or pressure is sufficient to cause a gas-phase chain reaction accompanied by branching to accelerate from a moderate (or even negligible) rate to explosion. Similarly, a very small change, brought about by one means or another, in the total number of intermolecular linkages may change a three-dimensional polymer from a moderately viscous liquid to a gel having infinite viscosity.

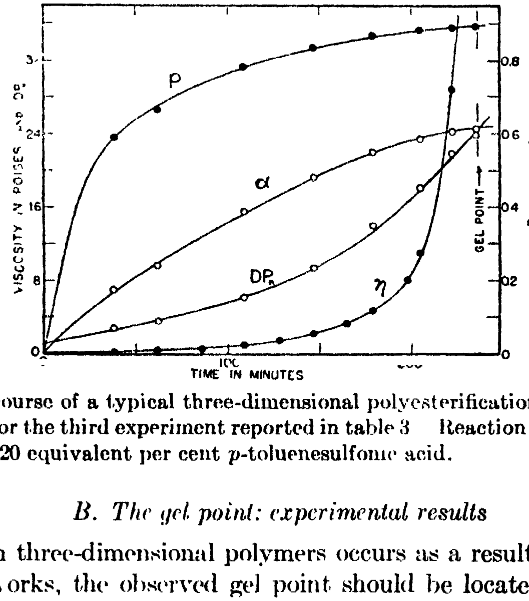


FIG 11. The course of a typical three-dimensional polyesterification (34). The results shown are those for the third experiment reported in table 3 Reaction conducted at 109°C. catalyzed with 0.20 equivalent per cent p-toluenesulfonic acid.

B. The gel point: experimental results

If gelation in three-dimensional polymers occurs as a result of the formation of infinite networks, the observed gel point should be located at the point at which α reaches its critical value, as defined by equation 18, except to the extent that theory is vitiated by neglecting intramolecular linkages. Experimental results on several three-dimensional condensation polymerizations confirm this postulate.

Kienle and Petke (51) observed that in the reaction of glycerol with an equivalent amount of succinic, adipic, or sebacic acid, gelation occurred at 76.5 ± 1 per cent esterification, i.e., at $p = 76.5$. If the differing reactivities of the hydroxyl groups of glycerol are neglected, equation 15 can be applied with $r = 1$ and $\rho = 1$. Hence, $\alpha_c = p^2 = 0.58$. Correction for the lower reactivity of the secondary hydroxyl would lower α_c somewhat. The theoretical value of α_c according to equation 18 is 0.50

The writer (34) observed the gel point in reactions of diethylene glycol with succinic or adipic acid and varying proportions of the tribasic acid, tricarballylic. Samples were removed from the reaction mixture at various intervals and titrated for unreacted carboxyl groups. The extent of reaction values (p) plotted against time, as in figure 11, were accurately extrapolated to the gel point, which was precisely observed by the sudden loss in fluidity as demonstrated by the failure of bubbles to rise in the mixture. Samples removed just prior to gelation were completely soluble in chloroform. Just after gelation they contained a small amount of gelatinous insoluble matter (gel) which remained suspended in the solvent. The viscosity of the mixture was also measured (figure 11). α was calculated from the proportions of ingredients (r and ρ) and from the extent of esterification of the carboxyl groups, p_A, using equation 15′. The number-average degree of polymerization $\overline{DP}_n$, calculated from the relationship (34)

$$\overline{DP}_n = \frac{\text{Number of units}}{\text{Number of molecules}} = \frac{f(1 - \rho + 1/r) + 2\rho}{f(1 - \rho + 1/r - 2p_A) + 2\rho} \tag{19}$$

is not very large nor is it increasing rapidly at the gel point. This merely means that at the gel point many molecules are still present; it does not preclude the

TABLE 3

Gel points for polymers containing tricarballylic acid

ADDITIONAL INGREDIENTS, DIETHYLENE GLYCOL AND	$\frac{\text{COOH}}{\text{OH}}$	ρ*	p AT GEL POINT		$\alpha_{\text{obsd.}}$ AT GEL POINT
			Observed	Calculated†	
Adipic acid..	1.000	0.293	0.911	0.879	0.59
Succinic acid	1.000	0.194	0.939	0.916	0.59
Succinic acid..	1.002	0.404	0.894	0.843	0.62
Adipic acid...... .	0.800	0.375	0.9907	0.955	0.58

* ρ = 3 × [tricarballylic [illegible]/[total carboxyl groups].

† Calculated from equati[illegible] when α = 1/2.

formation of [illegible] amount of indefinitely large structures at or beyond the gel point.

Other similarly obtained results are summarized in table 3. In every case the observed gel point is reached at higher than the theoretical extent of reaction. In the polymerization of pentaerythritol (f = 4) with an equivalent quantity of adipic acid gelation occurs at $\alpha = p^2 = 0.366$, compared with the theoretical $\alpha_c = 0.333$. The discrepancies are believed to be due to the failure of the theory to take into account a minor degree of intramolecular condensation. In effect, some of the inter-unit linkages are wasted in forming these intramolecular connections. Hence, the reaction must be carried somewhat farther to reach the critical point. Nevertheless, there is sufficient correlation between the approximate theory and experiment to confirm the hypothesis that gelation is caused by infinite networks.

C. *Molecular-weight distribution in three-dimensional polymers*

Three-dimensional polymers can be obtained from numerous combinations of bi- and multi-functional units of various types. A completely general treatment of the size-distribution problem is impractical, therefore. Rather, separate size-distribution expressions have been derived for various more or less general types of three-dimensional polymers. The fact that these possess a number of characteristics in common facilitates a unified discussion of the constitution of three-dimensional polymers.

The writer (35, 36) derived size-distribution relationships for tri- and tetrafunctional types, employing as assumptions those given above. Guided somewhat by the form of these size-distribution expressions, Stockmayer (87) succeeded in deriving more general distribution equations for various polymers in which the branching unit is f-functional. The statistical-mathematical derivations of these equations will not be repeated here. We shall be concerned solely with their physical interpretation.

The simplest possible type of three-dimensional polymer is that in which all units are of the same functionality f and in which all functional groups possess the same reaction probability p. (That is, if A groups of one monomer condense with B groups of another monomer, these are to be present in equivalent quantities in order that p_A shall equal p_B.) An example would be the condensation of a trihydric alcohol with an equimolar proportion of a tribasic acid, the hydroxyl groups of the former and the carboxyl groups of the latter being equally reactive. Or, both reactants might be tetrafunctional. Another example, a somewhat hypothetical addition type, would be provided by a pure triglyceride of a drying oil acid, each acid radical of which is capable of undergoing dimerization with another acid radical, to the total exclusion of other polymerization reactions. Still another example may be found in phenol–formaldehyde condensations in which the phenol is exclusively trireactive, as shown in table 1. Here it is necessary to regard the phenol as the structural unit, the formaldehyde merely supplying the inter-unit linkage. To obtain the weight distribution it then becomes necessary to assume that the molecular weight of a given species is proportional to the number of phenol residues which it contains. This approximation may distort the low-molecular-weight portion of the distribution curve.

For polymers of the above type Stockmayer (87) has derived the weight-distribution function

$$w_x = \frac{(1-\alpha)^2}{\alpha}\left[\frac{(fx-x)!f}{(x-1)!(fx-2x+2)!}\right]\beta^x \tag{20}$$

where f is the functionality of the unit(s), x is the number of units in the molecule, and β is defined by

$$\beta = \alpha(1-\alpha)^{f-2} \tag{21}$$

In accordance with the previous definition, α is the probability that one "leg" of a branch unit connects to another branch unit. In the present case $\alpha = p$, the extent of reaction, or the probability of reaction for any given functional group. An x-mer molecule with $x > 3$ can be constructed in various ways from x f-functional units ($f > 2$). Equation 20 combines all of these into a single w_x, regardless of the particular way in which the x units are connected.

The weight distribution prescribed by Stockmayer's equation (equation 20) for the trifunctional case ($f = 3$) is plotted in figure 12 for several stages of the condensation as indicated by α. In contrast to the weight-fraction distribution for linear condensation polymers, the curve shows a monotonic decrease with increase in size x. In other words, monomers always are present in greater amount, even on a weight basis, than species of any other (finite) size; x-mers are more abundant than $(x + 1)$-mers, etc. As the reaction progresses, i.e., as α increases, the distribution curve falls less steeply with increasing x; w_x's for the larger species increase with α. Even at the gel point, which according to equation 18 should occur at $\alpha = 1/2$, the curve displays a continuous decrease approaching zero as x proceeds toward infinity, and most of the material is present in polymers of rather low degree of polymerization. The distribution becomes increasingly broad as the gel point is approached.

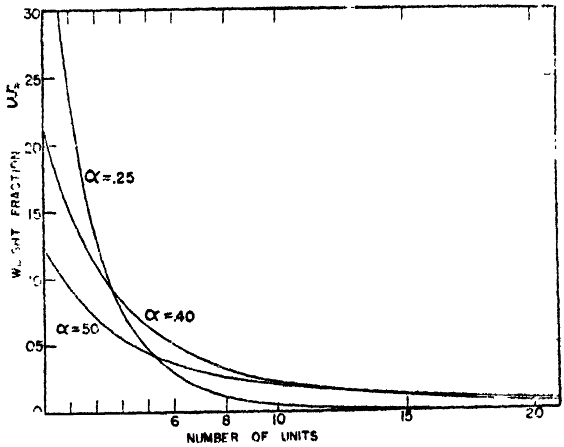


FIG. 12. Molecular-size distribution in a three-dimensional polymer. Polymers formed from trifunctional units at various stages of the condensation as indicated by α. Weight fraction vs. number of units x, as calculated from equation 20.

The progressive change in polymer constitution as the reaction progresses can be shown in another way by plotting weight fractions of various polymers against the extent of reaction $p = \alpha$. Plots of this type are shown in figure 13, calculated again from equation 20 with $f = 3$. Obviously, the amount of monomer must decrease continuously as the condensation progresses. Dimer begins to form at once, reaches a maximum amount near $\alpha = 0.2$, and then decreases as the condensation continues. Trimer formation does not set in at once, owing to the fact that it is a secondary product formed from dimer. Its curve reaches a maximum somewhat later—near $\alpha = 0.3$—and then decreases. Curves for tetramers (two tetramer structures are possible, but both are included in w_4 from equation 20) are similar; the maximum comes later. In no case, however, does the maximum occur beyond the gel point $\alpha = 1/2$.

The region beyond the gel point also is included in figure 13. The per cent gel curve and other features of polymer constitution in this region will be discussed later. It is sufficient to note here that the curves representing weight fractions of various species continue through the gel point without discontinuity.

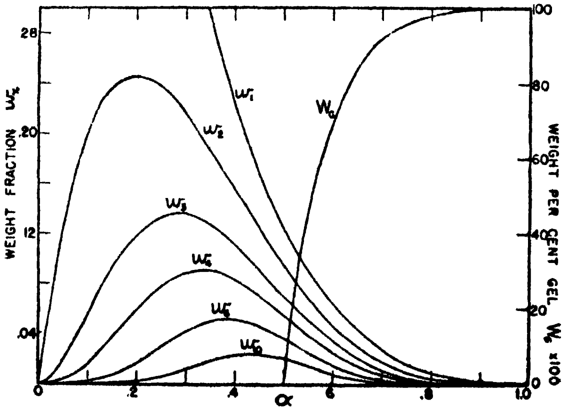


FIG. 13. Weight fractions of various species in a simple trifunctional condensation as a function of α, which in this case equals the extent of reaction p. The weight fraction of gel, W_g, is calculated from equation 29′.

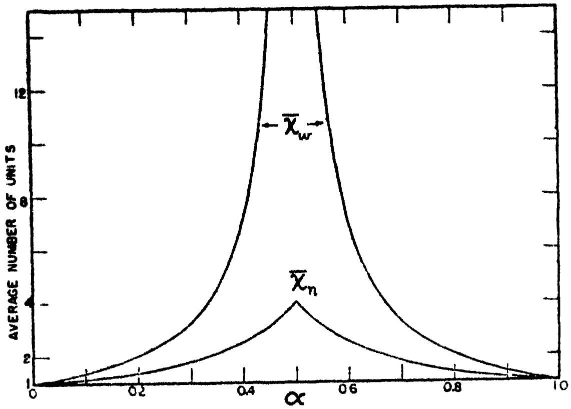


FIG. 14. Number-average, $\bar{x}_n$, and weight-average, $\bar{x}_w$, number of units per molecule in a simple trifunctional condensation as a function of α. Calculated from equations 22 and 23 with $f = 3$.

It can readily be shown that the number-average value of x is given by

$$\bar{x}_n = \overline{DP}_n = 1/(1 - \alpha f/2) \tag{22}$$

for the simple f-functional case presently under consideration. The weight average of x, found by summing over equation 20, is

$$\bar{x}_w = \Sigma x w_x = (1 + \alpha)/[1 - (f - 1)\alpha] \tag{23}$$

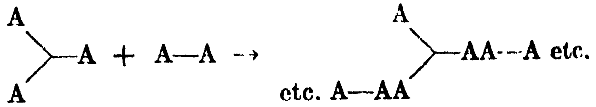
These averages are plotted against α in figure 14 for $f = 3$. As the reaction progresses the number average increases, but more slowly than does the weight average. At the gel point the number-average molecular weight has increased only fourfold; i.e., there are one-fourth as many molecules as were present initially. This is in accordance with the comparatively low molecular weights which have been observed (54) for three-dimensional polymers at their gel points.

The weight-average degree of polymerization increases more rapidly as the reaction progresses, running to infinity at the gel point. This is true in spite of the fact that precisely at the gel point only finite species are present, according to the distribution equation. (Only when α exceeds the critical value by a finite amount does the theory permit the existence of infinite networks.) The progression of the melt viscosity to infinity (see figure 11) as the gel point is approached is readily explained, inasmuch as melt viscosity generally depends on weight-average molecular weight (29).

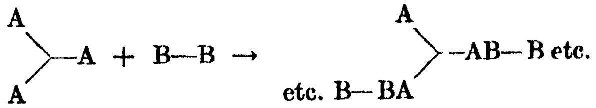
The ratio of $\bar{x}_w$ to x_n frequently has been proposed as an index of the heterogeneity of polymers. At the gel point this ratio becomes infinite, which is further indication of the extreme heterogeneity of three-dimensional polymers at the gel point.

The portion of figure 14 beyond the gel point will be discussed later.

For the condensation of f-functional units with bifunctional units, e.g.,



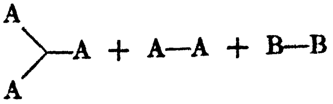
or



where A and B are present in equivalent amounts, Stockmayer (87) has derived the number-distribution equation

$$N_{n,l} = fN_0\rho^{n-1}(1-\rho)^l p^{n+l-1}(1-p)^{fn-2n+2} \times \frac{(fn-n+l)!}{n!\,l!\,(fn-2n+2)!} \tag{24}$$

where $N_{n,l}$ is the number of molecules in the polymer which contain n f-functional and l bifunctional units, N_0 is the number of f-functional units in the entire polymeric mixture, ρ is the ratio of the functional groups on branch units to the total number of functional units, and p again is the extent of reaction. Stockmayer (87) similarly has derived an expression for the distribution of "n, l, s-mers" formed from three reactants, one of them f-functional, the others bifunctional, e.g.,



This type includes the polyesters, such as were employed in the gelation experiments previously discussed (see table 3). These equations are difficult to apply, inasmuch as they contain more than one size variable; e.g., the molecular weight depends on *both* n and l in equation 24.

When the chains between the f-functional branch units are long—for example, when the proportion of branch units is small and, hence, the average number of A—A and B—B units between branch units is large—the above equations can be replaced approximately by a more tractable distribution function (87):

$$W_n = 2(1 - \alpha)^2 \frac{(fn - n + 1)!\beta^n}{n!(fn - 2n + 2)!} \tag{25}$$

where W_n is the weight fraction of molecules composed of n branch units, regardless of individual lengths of chains between branch units. Hence, equation 25 gives a "complexity" distribution rather than the actual size distribution. β is defined as in equation 21, and α again is the branching expectancy calculable from equations such as 15, 16, or 17.

When $f = 3$, equation 25 reduces to the equation previously derived by the writer (35)

$$W_n = (1 - \alpha)^2 \frac{(2n + 2)!}{(n + 1)!(n + 2)!} \beta^n \tag{26}$$

or

$$W'_z = (1 - \alpha)^2 \frac{(z + 1)!}{[(z + 1)/2]![(z + 3)/2]!} \beta^{(z-1)/2} \tag{26'}$$

where z, the number of chains per molecule, is related to n by the equation:

$$z = 2n + 1$$

(z is necessarily an odd integer.)

The similarity between these complexity distribution equations (equations 25, 26, and 26′) and the size-distribution equation (equation 20) for the simple f-functional case is apparent. If the weight fractions of polymers containing 0, 1, 2 . . . n, etc. branch units, or the corresponding weight fractions W'_z of polymers composed of 1, 3, 5 . . . z, etc. chains, are plotted against n, or z, the complexity curves so obtained are very similar in character to the *size* distribution for the simple f-functional case in figure 12.

To obtain the actual molecular-weight distribution in the present case it is necessary to take into consideration the variation in the lengths of the individual chains. These will vary according to the distribution previously derived for linear polymers (see equation 10). Thus, with reference to the "z" distribution of equation 26′, single chains, present in weight fraction W'_1, will cover a broad range of sizes. Similarly, W'_3 includes polymers varying considerably in total size, although the size distribution for $z = 3$ polymers is less than for the $z = 1$ polymer; etc. To obtain the weight fraction w_x of species composed of x units, regardless of the number of chains z, it is necessary to add together the weight fraction of $z = 1$ molecules having x units, the weight fraction of $z = 3$ molecules having a combined total of x units in their three chains (including the branch unit), etc. This operation can be simplified mathematically to the extent that calculation of the actual size distribution becomes feasible (35).

Figure 15 has been constructed for the purpose of showing the effect of $f = 3$ branching units on the distribution. The calculations have been made for chains having an average length of fifty units. The $\alpha = 0$ curve, for linear chains in the total absence of branch units, has been calculated from equation 10 with $p = 0.98$. The other curves represent bifunctional condensations to which have been added small amounts of trifunctional units such that $\alpha = 0.25$ and 0.50, respectively, when the reaction has been carried to the point where each contains an average of fifty units per chain. These curves do not represent successive stages of a given polymerization; *both* α and the average chain length increase as the condensation of given proportions of bi- and tri-functional units progresses. They are merely intended to show the dependence of the shape of the distribution curve on the degree of branching, α.

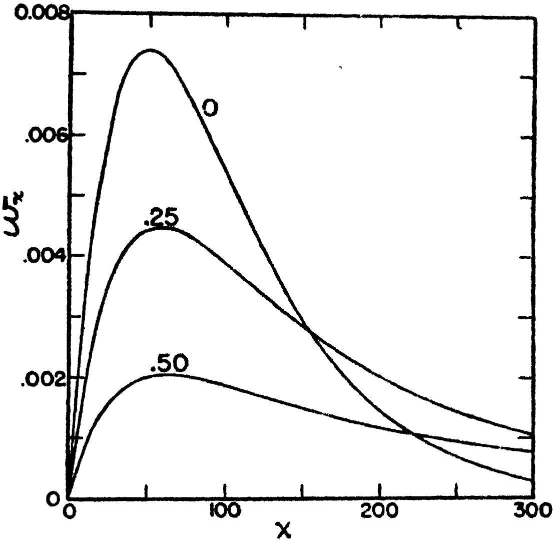


FIG. 15. Weight-fraction distributions vs. number of units for various degrees of trifunctional branching at constant average chain lengths of fifty units in each case. The curves represent $\alpha = 0$ (no branching), $\alpha = 0.25$, and $\alpha = 0.50$ (critical point).

The area under each of these curves extended to infinite x is the same. The position of the maximum is shifted comparatively little by increase in α (i.e., by increasing the proportions of trifunctional units), but the height is decreased. The quantity of high-molecular-weight material increases at the expense of lower polymers in such a way that the distribution curve is broadened as α increases. The weight-average degree of polymerization $\bar{x}_w$ at the gel point ($\alpha = 1/2$) again is infinite. The number-average molecular weight at the gel point is only three times the average molecular weight per chain.

These general principles apply similarly to three-dimensional addition polymers (36, 37, 88), such as those formed in the copolymerization of vinyl and divinyl reactants. They are also applicable to cross-linking of long polymer chains, such as occurs in the vulcanization of rubber, and to the phenomenon of protein gelation (37) under certain conditions.

D. Conversion of sol to gel

There is nothing in the derivations of the various distribution equations which limits them to the region up to the gel point. In a simple f-functional condensation, for example, it is obvious that the weight fraction of monomer is always equal to the probability that all of the f-functional groups of a given monomer unit are unreacted, i.e.,

$$w_1 = (1 - p)^f = (1 - \alpha)^f$$

which can also be obtained by setting $x = 1$ in equation 20. The weight fraction of dimers can be deduced directly as the probability that one, and only one, functional group of the unit has reacted, multiplied by the probability that the remaining $f - 1$ functional groups of the attached unit are unreacted.

$$w_2 = f\alpha(1 - \alpha)^{f-1}(1 - \alpha)^{f-1} = f\alpha(1 - \alpha)^{2f-2}$$

Clearly, these derivations place no restrictions on α, except that it be in the physically real range from zero to unity. Hence, these weight fractions, as well as those for higher species obtained from equation 20, should apply equally well before and after the gel point. The same reasoning can be applied in the case of branched polymers with long chains.

It is true that these expressions are somewhat inaccurate, owing to the disregard of intramolecular reactions. This approximation will be more serious the larger the molecule. There is relatively little likelihood of intramolecular reaction in monomers, dimers, and other lower species (except, of course, where formation of a ring of five, six, or sometimes seven members is possible). Thus, as α increases toward the gel point and larger species are formed, this approximation becomes increasingly important Obviously, the infinite network will contain intramolecular linkages (which, in fact, are responsible for the many circuitous connections and, hence, net-like structure of the gel fraction), and these will become more abundant in the gel fraction as α increases. If it were necessary to make the approximation that intramolecular reactions are totally excluded, the theoretical treatments would be of little value much beyond the gel point. This is not the case. The distribution equations actually include only the species of finite size. They are essentially oblivious of infinite networks. This is inherent in their derivation (35, 36). Hence, in deducing these distribution equations it was necessary merely to assume, or rather to make the approximation, that no intramolecular reactions occur *within finite species*. No reservations for infinite networks were necessary.[1]

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[1] The interpretation given here follows closely the one originally presented by the writer (35, 36, 37). Stockmayer (87) originally questioned the validity of this literal application of the distribution equations beyond the gel point. In the present discussion the writer has attempted to express the fundamental logic of the procedure more clearly, employing for the most part Stockmayer's more general distribution equations to illustrate the conclusions.

Upon examining the various distribution equations for three-dimensional polymers (see equations 20, 25, and 26) each is found to consist of three factors: a function of α, a function of f and the size variable x or n, and β^x, or β^n. If the sum of the weight fractions of all finite species (infinite species are not included in the equations, as already mentioned) is taken, the first of these factors can be placed outside the summation. If, for example, the simple f-functional case is considered, then upon introducing equation 20:

$$\sum_{\text{all finite } x} w_x = \frac{(1-\alpha)^2}{\alpha} \sum_{x=1}^{\infty} \left[\frac{f(fx-x)!\beta^x}{(x-1)!(fx-2x+2)!} \right] \tag{27}$$

β is a function of α (see equation 21) such that it possesses a maximum at $\alpha = \alpha_c$, the critical value of α (see equation 18). For all other permissible values of β there are two values of α which satisfy equation 21 one of them less and the other greater than α_c. The above summation on the right is equal to $\alpha'/(1-\alpha')^2$, where α' is the lower root of equation 21 for the given value of β; that is, where $\alpha' < \alpha_c$. Hence, the sum of all w_x's is equal to unity when $\alpha = \alpha' < \alpha_c$.

If, on the other hand, the reaction has progressed beyond the gel point so that $\alpha > \alpha_c$, then Σw_x will be less than unity. The summation on the right of equation 27, since it does not contain α explicitly, again will equal $\alpha'/(1-\alpha')^2$, where α' is the lower root of equation 21 for the given value of β. In other words, this summation is the same for either value of α, namely $\alpha > \alpha_c$ or $\alpha' < \alpha_c$, since both α and α' give the same value of β. But the function of α occurring before the summation is different for α and α'. Hence, when $\alpha > \alpha_c$ the sum of all weight fractions of finite species is given by

$$W_s = \Sigma w_x = \frac{(1-\alpha)^2\alpha'}{(1-\alpha')^2\alpha} \tag{28}$$

which is less than unity. This is the weight fraction of sol, or soluble species in the polymer. The summation is less than unity, owing to the presence of infinite networks not included in the distribution equation. The weight fraction, W_g, of these infinite networks, or gel, can be obtained by difference:

$$W_g = 1 - (1-\alpha)^2\alpha'/(1-\alpha')^2\alpha \tag{29}$$

When the units are trifunctional, according to equation 21 $\alpha' = (1-\alpha)$. Hence (87),

$$W_g = 1 - (1-\alpha)^3/\alpha^3 \tag{29'}$$

where $\alpha > \alpha_c = 1/2$. The weight percentage of gel calculated from this equation is plotted in figure 13. Its formation commences abruptly at the critical point, rises rapidly, and proceeds to 100 per cent as α goes to unity, i.e., as the reaction proceeds to completion.

It follows similarly from the form of the distribution function (25) for the complexity distribution in polymers composed of long chains joined by f-functional units that in this case

$$W_g = 1 - (1-\alpha)^2/(1-\alpha')^2 \tag{30}$$

where α and α' are roots of equation 21 with $\alpha > \alpha_c$ and $\alpha' < \alpha_c$. In the trifunctional case this reduces to

$$W_g = 1 - (1 - \alpha)^2/\alpha^2 = (2\alpha - 1)/\alpha^2 \tag{30'}$$

where $\alpha \geqslant 1/2$. The weight fraction of gel proceeds to unity somewhat less rapidly with increase in α than in the previous case, but otherwise the sol-to-gel conversion is similar.

It is interesting to examine the molecular-weight distribution in the sol fraction beyond the gel point. As is evident from the above discussion, the distribution function at some value $\alpha > \alpha_c$ is the same as for the conjugate value $\alpha' < \alpha_c$, except for the previously mentioned factor in the distribution function, which is an explicit function of α. This factor, which in the distribution function (20) occurs as $(1 - \alpha)^2/\alpha$, is less for α than for α', but it is the same for species of all sizes, or complexities. In a simple f-functional condensation, therefore, the same size distribution prevails *within the sol fraction* at $\alpha > \alpha_c$ as occurred for the entire polymer earlier in the condensation when the extent of reaction corresponded to α', where α' and α are roots of equation 21 for the same value of β. Only the absolute amounts of each species are smaller, and these are all reduced by the same factor W_s. Consequently, the distribution curves in figure 12 apply also to the sol after gelation at the respective α values 0.60 and 0.75.

Inasmuch as the molecular-weight distribution always approaches zero as x becomes very large, it is clear that the demarcation between sol and gel is by no means an arbitrary distinction. Extremely large ("almost infinite") molecular species, which might be regarded as intermediate between sol and gel, are never present in more than infinitesimal quantity. The structural distinction between sol and gel is as well defined as that between a liquid and its vapor, notwithstanding the physical interspersion of sol in gel.

In the course of a simple f-functional condensation polymerization larger species gradually are formed at the expense of smaller molecules. The distribution broadens, as shown in figure 12, reaching a maximum degree of heterogeneity at the critical point. Here infinite networks suddenly make their appearance (see figure 13). Gel increases at the expense of sol as the condensation continues. The sol which remains decreases in average molecular weight, owing to the preferential conversion of the larger, more complex, species to the infinite network fraction. The molecular-weight distribution of the sol retraces in the reverse direction the exact course followed by the polymer up to the gel point. Weight and number averages of the sol exhibit a corresponding retroversion, as is shown in figure 14.

Other types of three-dimensional polymers (35, 36) behave similarly as they pass beyond the gel point. In the case of occasionally branched long chains formed by condensation of bifunctional and f-functional units, the complexity distribution of the sol after gelation reverts over the same course traversed up to the gel point (35), as can be shown from equation 25. Thus for $f = 3$, the *complexity* distribution of the sol is the same at $\alpha = 0.7$ as prevailed for the polymer as a whole when $\alpha = 0.3$. However, as the condensation progresses in this case there is an increase in the average chain length as well as in α. Consequently the molecular weight averages for the sol at $\alpha = 0.7$ will be greater than those at $\alpha = 0.3$ in proportion to the increase in the average chain length.

So far, experiments to determine the actual course of the conversion of sol to gel in a quantitatively observed condensation polymerization have not been reported, nor has the predicted decrease in complexity of the sol with increase in α been verified. It is to be expected that results of this nature will differ somewhat from the theoretical predictions, owing to the occurrence of intramolecular condensations within finite species. The observed gel points, as was shown above, occur somewhat beyond the calculated critical values on this account. The greatest departure from the approximate theory should, in fact, occur at the critical point. It is to be expected that in order to depict actual condensations it will be necessary to distort the α scales of diagrams such as figures 13 and 14. The gel point will have to be shifted to slightly larger α's (as here calculated), the curves on the left (prior to gelation) being expanded and those on the right compressed in such a way that the greatest distortion occurs near the critical α.

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ERRATUM

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Page 398: The first sentence in the second paragraph under Section H should read: "The concentration of ferric iron in plasma averages about 100–200 γ per 100 cc. of plasma (54)."

THE STATUS OF PLANT-GROWTH SUBSTANCES AND HERBICIDES IN 1945

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I. INTRODUCTION

During the past ten or twelve years, numerous investigations into the preparation, properties, and effects of plant-growth substances have been conducted. Many of the results obtained have been exceedingly interesting from a scientific point of view, as well as very valuable economically. In more recent years it has been observed that some of the growth-producing substances, when applied under different conditions of concentration and temperature, become effective herbicides for certain species of harmful plants.

In view of the importance of this line of work, a literature survey of the more important recent contributions has been made.

It has been known for many years that illuminating gas in the air, even in small amounts, is toxic to plants (30, 63, 64, 119, 120, 135, 153, 161), the damage depending not only on the amount of gas present but also on the species of plant involved. One of the most noticeable effects on the plant is epinasty, a bending or distortion caused by a differential growth rate, usually in the leaf petiole. In an investigation of this problem, Zimmerman *et al.* (172) found that ethylene, present in illuminating gas in small amounts and responsible for the epinastic effect, may enter the plant through the stem, petiole, or leaf blade and spread throughout the entire plant. Should but a single leaf be exposed to ethylene, the remainder of the plant will also show the epinastic response. It is not known exactly how this particular response is transmitted, but it is believed to be through the intercellular spaces. Ferri (34) has shown that growth substances applied to the base of cuttings are transmitted upward through the xylem. Beal (8) uses the word "telemorphic" to describe the effect, on one part of the plant, of a growth substance applied at another part.

Doubt (3) reported that when illuminating gas was passed through soil in which tomato plants were growing, there was a tendency for the roots to grow out of the soil. There was also an unusual development of the basal part of the stem. Zimmerman *et al.* (161) verified these results and, in so doing, came to the conclusion that the root stimulation was due to the presence of carbon monoxide in the illuminating gas. They therefore exposed portions of stems to concentrations of carbon monoxide (162) and found that, in addition to the epinastic and other effects usually produced, the gas induced definite rooting responses in twenty-seven species of plants. This was the first report to show that new organs could be induced by the application of a known chemical.

More work on carbon monoxide (163) and other gases (164) followed, and it was soon found that ethylene, acetylene, and propylene in the proper concentrations were also effective in stimulating root growth. The fact that more than one pure chemical substance was able to induce a formative response naturally raised the question as to how many other chemicals were capable of performing the same function. Went (149) reported a root-forming substance in plants which he called rhizocauline and which formed roots on treated cuttings of sweet pea. He also reported a test method by which the concentration of rhizocauline could be determined by the number of roots formed. Thimann and Went (146), using this assay method, determined the comparative amounts of the root-forming substance occurring naturally in plant and animal material. Laibach *et al.* (93), using concentrates from urine and pollen mixed with lanolin and applied locally, induced increased root growth of cuttings. Kogl *et al.* (87) were the first to isolate a growth substance as a pure chemical compound and identify it as β-indoleacetic acid.

Hitchcock (66), in testing many chemicals, found that, in addition to indoleacetic acid, indolepropionic acid, phenylacrylic acid, and phenylpropionic acid were effective in causing root initiation. Within a short time, eight new chemical compounds were found to have special effects on plants. These, as reported by Zimmerman and Wilcoxon (175), were α-naphthaleneacetic acid, β-naphthaleneacetic acid, acenaphthyl-5-acetic acid, indolebutyric acid, phenylacetic acid, fluoreneacetic acid, anthraceneacetic acid, and α-naphthylacetonitrile. It was also determined (68) that a rooting response would follow if any of these substances were added to the soil in which a plant was growing. At this point several papers appeared substantiating the findings concerning growth substances in inducing root initiation (16, 18, 67, 92, 101, 165), and numerous articles were published in semiscientific and popular magazines. β-Indoleacetic and β-indolebutyric acids appeared on the market as the powdered hormone in talc or other dry inert material for dusting on the ends of cuttings, and also dissolved in lanolin in the salve form.

Haagen-Smit and Went (57) and Thimann (141) criticized the work of Zimmerman and his associates on the grounds that the experiments had been carried out on green hormone-rich material in light, and that the acid effect of the compounds, which might interfere with the transport of the growth hormones already in the plant, had not been considered. In answer to this criticism, Zimmerman *et al.* (174) reported that nine esters must be added to the list of growth substances, and that some of these were more effective than the original "hetero-auxin", β-indoleacetic acid, isolated from plant tissue. The nine esters included methyl and ethyl α-naphthaleneacetates, methyl and ethyl phenylacetates, *n*-butyl and isobutyl phenylacetates, methyl β-indoleacetate, methyl β-indolebutyrate, and methyl β-indolepropionate.

With esters of the indole and other acids as effective as the acids themselves, it was a natural step to try the effect of their salts. Not all tests were successful, but in a number of cases certain of the salts were more potent in initiating root growth than were the corresponding acids (45, 166). The salts known at this time to be effective were the potassium, sodium, calcium, barium, strontium, ammonium, trimethylammonium, and tetramethylammonium salts of naphthaleneacetic acid; the potassium, sodium, ammonium, trimethylammonium, and tetramethylammonium salts of β-indoleacetic acid; the potassium, sodium, ammonium, trimethylammonium, and tetramethylammonium salts of γ-indolebutyric acid; the potassium and sodium salts of indolepropionic acid; and potassium phenylacetate. Zimmerman and Hitchcock (167) in 1939 reported twenty-six new growth substances[1] in an article describing the effect of growth substances used in the vapor form. They also noticed that some of these caused parthenocarpic development of holly berries, of Fuschia and orchid ovularies, and the enlargement of the receptacle of strawberries.

This additional effect of a growth substance, whereby the development of the ovulary is stimulated in the absence of fertilization, leads to an entirely new use for these synthetic organic acids and their esters and salts. It becomes necessary to go back again in the literature and lead up to this point, inasmuch as the parthenocarpic development of fruit by plant extracts had been known for some time.

The observation that pollen contains substances which stimulate the enlargement of the ovulary, apart from the fertilizing function of the pollen nucleus, was made in 1902 by Massart (107) and in 1909 by Fitting (35, 36). In 1918 Morita (112) repeated some of Fitting's experiments and attempted the stimulation of ovulary development with several organic chemicals. In 1932, Laibach (90) further verified Fitting's work and also found that in animal tissue there were hormones that would induce development of the plant ovulary. In 1934 and 1935 Yasuda (155, 156, 157) injected aqueous pollen extracts into plant ovularies and obtained, in some cases, normal-sized but seedless fruit. Gustafson (49) also achieved parthenocarpy by means of pollen extracts applied to the pistil. He later (52) showed that the growth-promoting substance content in the ovularies of flower buds from parthenocarpic varieties of oranges, lemons, and grapes is higher than in the ovularies from corresponding varieties that do not produce fruit parthenocarpically. In 1936 Gustafson (48) caused fruits to develop parthenocarpically in several species of plants by treating the pistils with known chemical compounds already found effective in stimulating the formation of roots. He thereby opened another field to the investigators of growth-promoting substances.

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[1] Ethyl α- and β-naphthoxy-α-butyrates, methyl and ethyl α- and β-naphthoxyacetates, α- and β-naphthaleneacetic acid picrates, butyl and isobutyl phenylacetates, β-naphthoxyacetamide, β-naphthoxy-α-butyric acid, α-naphthoflavone, α-naphthylamine, methyl ethyl phenylethylmalonate, phenylbutyric acid, phenylethylacetic acid, *N*-phenylglycine ethyl ester, irradiated methyl *m*-nitrocinnamate, methyl α-trimethylamino-β-(3-indole)propionate iodide, ethyl α-bromoacetoacetate, homopiperonylic acid, nicotinic acid nitrate, pimelic acid, and *m*-tolyl-β-napthoxyacetate.

The following year, Gardner and Marth (40) induced parthenocarpy in holly and strawberries by spraying with growth-promoting chemicals, and in a similar manner Hagemann (58) and Schroeder (126) brought about parthenocarpy in gladiolus and tomatoes, respectively. Since 1937 research on the practical application of growth substances to greenhouse and truck crops has been carried on by many workers, including Gustafson (50, 51). Wong (154) produced parthenocarpic watermelons, cucumbers, and peppers, and Burrell and Whitaker (14) parthenocarpic muskmelons, but it has been only with the tomato that much success has been obtained (81, 82, 83, 115, 124, 137). This, however, has been phenomenal, and the use of growth-promoting chemicals on greenhouse tomatoes has increased to such an extent that in 1945 in Ohio, approximately 1,800,000 plants were treated, or about half the tomato plants grown in greenhouses in the state (85).

Closely associated with commencement of ovulary growth is the prevention of the formation of an absciss layer between it and the pedicel. Preventing this absciss layer from forming may even be the first step in fruit formation. Abscission may take place at any time between the withering of the flower and the maturation of the fruit. To horticulturalists it is a well-known fact that many fruits which have started in their development, drop before maturity. Dorsey (29) and others associated this with the lack of seed development. Laibach (91), La Rue (94), and Myers (118) have shown that if the debladed petioles of many plants are treated with growth substances, they will not drop nearly so soon as those not treated. Gardner *et al.* (41, 42) demonstrated that spraying nearly mature apples with growth-promoting substances prevents them from dropping. The subject of a pre-harvest spray for apples and other fruits was then taken up by several of the agricultural experiment stations (3, 12, 15, 19, 31, 32, 33, 38, 39, 46, 65, 73, 74, 76, 77, 98, 113, 116, 117, 122, 123, 129, 131, 132, 133, 134), with the result that the pre-harvest spray now is recommended to the fruit grower, especially for early apples. However, so much varietal difference has been found in the response of apples to treatment that recommendations vary in different parts of the country, and the grower is advised to consult his own state agricultural experiment station for spraying directions.

In addition to the stimulation of root formation, fruit formation, and petiole growth to prevent premature fruit drop, one other type of plant-tissue stimulation due to organic chemicals occurs which can be put to practical use. This is the stimulation of bud or shoot development. Although, according to Howlett (85), results are quite pronounced, this phase at present has not been exploited commercially, because in general there appears to be no particular benefit in stimulating the growth of buds. It has been shown that potato tubers can be induced to send out shoots at a time when normally they would be inactive, owing to the rest period. Experiments (21, 22, 24, 27, 28, 138, 151, 167) conducted over a number of years with the vapor of ethylene chlorohydrin and with sodium, potassium, and ammonium thiocyanates, and a few other chemicals have demonstrated that these have an unusual physiological effect on dormant potato tubers and will shorten the normal rest period.

It would seem paradoxical that growth substances which exert a promotive effect on the growth of stems and petioles, and initiate root formation, should in concentrations of the same order of magnitude exert exactly the reverse effect on the growth of roots. However, it has been shown by Bonner and Koepfli (10) that the chemical specificity of the growth substance that will promote stem growth is closely similar to the chemical specificity that will inhibit root growth. The inhibition of root growth has been recorded several times (87, 141, 142, 150).

There are other suppression or growth-prevention effects, all of which have an important utilitarian future. First is the removal of superfluous flowers and fruits, as opposed to the prevention of the pre-harvest drop of fruit. Second is the prevention of early bud development in stored potato tubers, as opposed to the breaking of the normal rest period. Third is the delay in the development of flower and leaf buds of early flowering trees and shrubs to prevent early frost damage, lengthen the period of time over which they blossom and fruit, and lengthen the period during which it is possible to plant shrubs in the spring, as opposed to the stimulation of flower and bud growth. Fourth is the differential herbicide. In this case, broad-leaved plants are stimulated to proliferate themselves to death while grasses are unaffected when both are treated with several times the concentration of growth substance that will cause the wanted stimulation of fruitfulness, petiole growth, or root formation.

Spraying apples to reduce the number of flowers setting fruit, and therefore making it unnecessary to thin by hand later in the season, was first shown to be feasible by Auchter and Roberts in 1933 and 1935 (1, 2). A number of articles have since been published on this subject, almost entirely from state agricultural experiment stations (4, 11, 13, 37, 44, 72, 75, 78, 79, 80, 84, 84a, 99, 100, 114, 125). In the first experiments on the thinning of fruit by spraying, tar oil distillates such as Reico were used. MacDaniels and Hildebrand (99) suggested the use of dinitro compounds, and Elgetol (sodium dinitro-*o*-cresylate), which acts as a pollenicide, Dow D-41 (dinitro-*o*-cylohexylphenol), and Dow D-145 (dinitro-*o*-cresol) gave promise of successful use. However, naphthaleneacetic acid, naphthaleneacetamide, and indoleacetic acid may be used for the same effect. Staymone and Hormex are now on the market to be used as a thinning spray or dust. Schneider and Enzie (125) found that naphthaleneacetic acid and naphthaleneacetamide as a 0.01 per cent spray at full bloom were too severe, nearly eliminating the crop; they recommended 0.002 per cent as a more favorable concentration. As in the case of the pre-harvest spray to prevent drop, the thinning spray is still in the advanced experimental stage and varietal, seasonal, and climatic differences exert such an influence that the general public has not been advised to use the thinning spray except under the supervision of an agricultural experiment station. Whether or not growth substances will be used commercially as thinning sprays depends upon what "follow-up" there is to the findings of Gardner (43), who sprayed apple trees with a wax emulsion only and found that it functioned as a thinning agent by providing a coating to the stigma, preventing the pollen from functioning. The obvious advantage of this is the lack of any possibly deleterious effect on the young foliage.

One of the first inhibition effects of indoleacetic acid noted was that of the retardation of bud growth (127, 141, 143, 144, 145). One practical side of this effect was made use of by Guthrie and others (23, 25, 26, 53, 54, 55, 56), who showed that potato tubers could be kept dormant by the use of the vapors of methyl α-naphthaleneacetate and other growth substances. A second practical use occurs in the treatment of rose bushes (102, 103), so that the period over which they may be shipped in the spring is considerably lengthened, and so that they will not sprout in winter storage. Another practical use for such growth substances is for retarding buds on fruit trees in order to prevent their being killed by late frosts, and to extend the fruiting season of certain varieties (69). In the latter case, the spray containing the growth substance (potassium α-naphthaleneacetate) is applied the summer before the effect is desired.

Prior to 1939, the known growth substances, excluding carbon monoxide, ethylene, and the other gases previously mentioned, consisted of the acids, esters, and salts of the naphthalene and indole compounds. A new growth substance, β-naphthoxyacetic acid, was first described as physiologically active in 1938 (86). In 1939 Bausor (5) detailed its synthesis and described its effects, and those of its potassium and sodium salts, on plants as compared to the known growth substances. They were found to be similar, but β-naphthoxyacetic acid was more powerful. In observing its effects on tomato plants (6,7), it was found to act in as short a period as 2 hr. and was able to produce detrimental formative effects at low concentrations. Zimmerman and Hitchcock (168) also reported the synthesis of β-naphthoxyacetic acid and described its formative effects on several plants.

Inasmuch as new growth substances were being found, there was a natural curiosity as to the minimum molecular structural requirements. Koepfli, Thimann, and Went (88) went so far as to give what they believed to be the minimum requirement as follows: (*a*) a ring system as nucleus, (*b*) a double bond in this ring, (*c*) a side chain, (*d*) a carboxyl group (or a structure readily converted to a carboxyl) on this side chain at least one carbon atom removed from the ring, and (*e*) a particular space relationship between the ring and the carboxyl group. These specifications would eliminate benzoic acid as an active compound, since the carboxyl group is not one carbon atom removed from the ring. Results by Zimmerman and Hitchcock (169) have shown that phenoxy compounds and substituted benzoic acids are active when bromine atoms and nitro groups are substituted in the proper positions in the ring. These substitutions do not change the space relationship between the carboxyl and the ring. However, the biological activity of hormone-like substances extends from simple molecules like carbon monoxide gas to complex structures like naphthaleneacetic acid. In spite of the minimum requirements laid down by

Koepfli *et al.*, a comparison of the molecular structures of active and inactive compounds shows that a satisfactory understanding of what constitutes a growth substance has not yet been reached.

Hitchcock and Zimmerman (70) also found the root-inducing activity of the phenoxy compounds to vary from low to very high, depending on the kind, number, and position of substituents in the ring, and on the relative length of the side chain. They had a relatively narrow effective range below that which is toxic, and overtreatment produced swelling, proliferation, and retarded growth of roots, which became extremely fasciated. An unusual result was found in the case of triiodobenzoic acid (170), which induced leafy shoots to grow flower clusters.

A leaf modification similar to that in virus-diseased plants was obtained when plants were treated with some of the active phenoxy (xylenoxy) acids having two methyl groups substituted in various positions in the ring (173). The effects, however, could not be transmitted by grafting or inoculation, as is true of virus diseases, and after the chemical influence had disappeared, the treated plants reverted to normal. Stoutmeyer (136) found that the addition of methyl, hydrogen, or isoprene groups in various positions on a growth substance does not interfere with the action in aiding root formation, and may even enhance it in some cases.

The use of growth substances as differential herbicides is recent, although chemicals have been used for killing weeds for many years. Iron sulfate and sodium chlorate are very effective in killing plants when applied as a spray but show little or no differential quality, grasses being killed nearly as readily as weeds. Ammonium sulfate and ammonium nitrate have also been used and, where applied in sufficient concentration, kill the weeds by osmotic action. The grass, because of its narrower leaves and internodal method of growth, often recovers from not too heavy applications and later is stimulated by the residual action of the nitrogen in the case of the ammonium sulfate and nitrate. Some differential effects have been obtained by the use of oil sprays in onion, carrot, and parsnip fields where, because of the waxy or finely divided character of the foliage, the vegetables suffer little injury (17, 89, 139, 159). Oil sprays have also been recommended for lawns (95, 96, 97), but control in this case is a matter of degree only; too concentrated an application injures the grass and too light an application does not give an effective kill of the broad-leaved weeds.

Westgate and Raynor (152) recommended Sinox (sodium dinitro-*o*-cresylate) as a non-corrosive, relatively non-hazardous, differential herbicide used for controlling annual weeds of cereals, flax, onions, alfalfa, corn, roadsides, and pastures. It will kill bent grass and therefore will not be used to any extent on lawns. It kills young crab-grass seedlings but does not prevent later germination. It is non-effective against deep-rooted perennials. On the other hand, one of the most effective chemicals for use against deep-rooted perennials, but of no use on lawns, is ammonium sulfamate (ammate).

When applied in concentrations of ¾ pound per gallon of water, ammonium sulfamate is found to be most effective for killing poison ivy (147, 158). The chemical penetrates to the roots, preventing sprouting after the top has been killed. The soil is not severely sterilized, as is the case with sodium chlorate, and grass may recover. Applications to ivy on trees will eradicate the ivy and not damage the tree, if the tree leaves are not sprayed. Grigsby (47) found that ragweed was destroyed by spraying with dinitro-2-butylphenol and with pentachlorophenol. Water solutions kill more slowly than kerosene solutions.

Formative effects were noticed to a greater or less extent in the earlier experiments on plant-growth substances, but with the synthesis of β-naphthoxyacetic acid (5, 6, 7, 86, 168) and the phenoxy compounds (70, 169) it was found that a slight increase in the concentration of these substances multiplied the formative effects to such an extent that a sprayed plant seemed to exhaust or destroy its food reserves and collapse in its entirety (61). The use of the more effective growth substances as herbicides naturally suggested itself (109). Hamner and Tukey (61) sprayed 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid on bindweed and obtained a complete kill down to the root tips. At approximately the same time similar articles by Hamner and Tukey (62) and by Marth and Mitchell (105) appeared, describing the effect of 2,4-dichlorophenoxyacetic acid as a differential herbicide on lawns. All plants growing on the lawns, with the exception of grasses, were destroyed with no noticeable ill effect on the grasses. Soon others corroborated these findings (9, 121, 128). Warm weather accelerated the rate at which the weeds were killed, but Marth and Davis (104) found that lawn weeds which had been sprayed in cold weather with little apparent effect died when the weather became warm.

2,4-Dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid are almost equally effective, according to Snyder (130), and 2,4,6-tribromophenoxyacetic acid, although not a plant hormone because of the fact that it causes no growth reaction, will kill poison ivy. Snyder, quoting a representative of the American Chemical Paint Company of Ambler, Pennsylvania, states that even more effective weed killers are to be put on the market. The present commercial product of the company is Weedone, which is very effective on a weedy lawn but at present commands a price that makes it impractical for use on a large area.

A rather unexpected reaction of 2,4-dichlorophenoxyacetic acid is its effect on the ripening of fruit (110). Ethylene has been used commercially for this purpose, but the plant hormone has several advantages over ethylene. The ripening period of bananas, apples, and pears was shortened by treatment with 2,4-D, but tomatoes, peppers, and persimmons were not affected.

Although plant-growth substances and related chemicals show great promise in ridding lawns of broad-leaved weeds, unfortunately some of the worst lawn weeds are grasses themselves, and show the same tolerance to 2,4-D as do the wanted lawn grasses. Crab grass, Nimble Will, goose grass, foxtail, and orchard grass are probably the worst offenders, with crab grass giving more trouble than the others combined. Weed seed, including that of crab grass, may be destroyed by cyanamid or chloropicrin prior to the seeding of a lawn, but these chemicals are not so useful on established turf, as they are toxic to all grasses (111, 148).

De France (20) found that when crab grass was treated at the time of seed formation with any of the following chemicals and preparations—sodium arsenite, sodium fluoride, sodium chlorate, Lawn Sinox, Milarsenite, "Gone with the Wind", and Zotox—there was a very substantial decrease in the percentage of germination of crab-grass seed. Control is largely a matter of the prevention of seed formation for reinfestation. If the season's crop of crab grass would germinate at one time, instead of having a prolonged period of germination from April until September, the plants could be killed in the seedling stage by one treatment which would not greatly harm the mature grasses, but many treatments are necessary if the successive crops of seedlings are to be eliminated. The logical time for treatment appears to be during the period of seed formation.

No one growth substance can be considered best for all purposes, although there is considerable overlapping. For convenience the different groups are taken separately and their values, as considered by Zimmerman (160), summarized.

II. PLANT-GROWTH SUBSTANCES

A. Naphthalene compounds

When properly applied, α-naphthaleneacetic acid and its derivatives inhibit bud growth, induce roots on cuttings, and prevent abscission layers from forming. An important use of α-naphthaleneacetic acid is for the prevention of preharvest drop of apples. Naphthalene compounds are frequently important in preventing the buds of tubers, bulbs, corms, cuttings, and trees from growing. After treatment with α-naphthaleneacetic acid, potatoes may be stored indefinitely without much shrinkage, and fruit trees can be prevented from flowering until danger of frost is past. The same treatment may be important in delaying the flowering of trees, so as to spread the fruit crop over a longer harvest period. This would apply particularly to tropical species, such as the mango and avocado. The flowering period of ornamental shrubs can be regulated to some extent. Wherever inhibition is desired, the α-naphthalene compounds appear to be the most effective. The β-isomers, as well as the higher homologs of α-naphthaleneacetic acid, are inactive.

B. Indole compounds

Indolebutyric acid appears to be of the most practical importance in this group. Its main use is in the propagation of plants, where it is used on cuttings to induce root growth. Although mixtures of naphthaleneacetic acid, chlorophenoxy compounds, and indolebutyric acid are now favored over a single substance for this purpose, indolebutyric acid remains the most important component of the mixture. Indolebutyric acid is also important in inducing fruit set and parthenocarpy in the tomato. Most commercial preparations now use for this purpose a mixture of indolebutyric acid and β-naphthoxyacetic acid.

The latter is much more active than the indolebutyric acid but has a tendency to induce unwanted formative effects.

C. Naphthoxy compounds

β-Naphthoxyacetic acid and its active higher homologs induce adventitious roots, cause plants to grow with modified organs, and induce seedless fruit. They are not so favorable for propagating plants from cuttings as indolebutyric acid, but for some species can be used effectively. β-Naphthoxyacetic acid is twenty to thirty times as effective as indolebutyric acid but not as active as dichlorophenoxyacetic acid in inducing parthenocarpy. From a scientific point of view the naphthoxy compounds are interesting because they induce formative effects when applied to growing plants. The growth which develops after treatment frequently shows leaves, stems, flowers, and fruit modified in size, shape, venation, and pattern. The similarity of the formative effects produced by naphthoxy compounds, substituted phenoxy compounds, and substituted benzoic acids to the effects produced by a plant virus brings up an interesting and untouched research problem as to the connection between the two. Plants with formative effects produced by the growth substances resume a normal habit of growth when the growth substance is no longer applied. It is not known whether or not formative effects produced by a plant virus are due to the production of growth substances by the virus.

D. Substituted phenoxy compounds

Substituted phenoxy compounds are proving to be perhaps the most effective of all growth substances. Zimmerman (160) gives the molecular configuration of eighteen such halogen-substituted phenoxy compounds which he found to be active in producing cell elongation and curvature. Bromo-substituted phenoxy compounds showed approximately the same activity as the corresponding chloro-substituted compounds.

Phenoxyacetic acid as such is but slightly active, but halogen-substituted phenoxy compounds are activated according to the positions and the number of substituted groups in the nucleus of the molecule.

The higher homologs of substituted phenoxyacetic acid are also very active. Nitro substitutions do not act in the same way as halogen atoms. The most active substituted phenoxy compounds for cell elongation are 2,4-dichlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid. The former has now come into commercial use as a differential herbicide, since it causes the death of broad-leaved weeds with little or no detrimental effect on the surrounding grasses.

Substituted phenoxy compounds are important for propagating plants, preventing pre-harvest fruit drop, inhibiting bud development, and inducing seedless fruit. For the latter response dichlorophenoxyacetic acid is the most effective compound yet discovered. For example, 10 mg. per liter of water as a spray is approximately optimum for inducing parthenocarpy and seedless fruit of tomatoes. This is in contrast to 3000 mg. per liter for indolebutyric acid and 100 mg. per liter for naphthoxyacetic acid.

When used as a vapor in a greenhouse with a volume of 2500 cubic feet, 5 mg. of methyl dichlorophenoxyacetate is sufficient to induce fruit set throughout the house.

For the propagation of plants, halogen-substituted phenoxy compounds are effective when used alone or in a mixture of other growth substances. A mixture extends the effectiveness of a preparation to include more species of susceptible plants. So far, no one substance used alone has been found effective on all species. Not all of the substituted chlorophenoxy compounds have the same formative influence on plants, and it has not yet been possible to determine what part of the molecule is responsible for a given response.

E. Substituted benzoic acids

The possible practical applications of the substituted benzoic acids have not been thoroughly investigated. It would seem, however, that any substance as active as the substituted benzoic group for regulating the growth of plants is certain to be useful. Enough has been done to show that when various combinations of halogen and nitro groups are substituted in the nucleus, the molecule is activated. Benzoic acid is physiologically inactive, but 2,3,5-triiodobenzoic acid has a pronounced formative influence on plants. 2-Bromo-3-nitrobenzoic acid is mildly active for cell elongation and very active for modification of organs. 2-Chloro-5-nitrobenzoic acid is inactive for cell elongation but modifies organs. Triiodobenzoic acid, as has already been stated, has a pronounced effect on the flowering habit of tomato plants, producing flower clusters at the end of the main branches in addition to those along the stem.

Synerholm and Zimmerman (140) gave directions for the preparation of substituted phenoxyalkylcarboxylic acids with details for testing them as plant-growth substances. They found that halogen atoms or methyl groups are of the most importance in lending activity to the phenoxyalkylcarboxylic acids. The 2-, 3-, and 4-positions in the benzene ring are those in which the substituents exert their greatest influence.

The activity of growth substances is usually detected by curvatures resulting from induced cell elongation, or by formative effects on later growth. The former response occurs within a comparatively short period of time, considered in terms of minutes or hours. Formative effects appear within a few days or weeks after the plant has had time to grow and produce new organs. If a chemical compound does not induce curvatures, cell elongation, or formative effects, it is considered inactive. Hitchcock and Zimmerman (71) published a method by which the effectiveness of growth substances could be measured.

Active chemicals are referred to by various investigators as growth regulators growth substances, auxins, or plant hormones. The latter term must be considered incorrect, since the synthetic substances, with the exception of cinnamic acid, ethylene, and indoleacetic acid, are not known to be identical with naturally occurring hormones.

Methods of treating plants with growth substances are varied. To induce roots on cuttings, the basal ends are dipped into powder preparations or solutions of the substance. The concentration requirements vary with the species, and for general use more than one strength is desirable. To prevent pre-harvest apple drop, a water solution containing 10–50 mg. of naphthaleneacetic acid per liter is sprayed on the entire tree at the time apples begin to fall prematurely.

To inhibit the growth of buds on tubers, bulbs, corms, rhizomes, trees, and shrubs, the plants or plant parts are exposed to vapors, dipped into solutions, sprayed with solutions, dusted with powder preparations, or otherwise treated with naphthaleneacetic acid or its derivatives. For inhibition by vapor treatments, methyl and ethyl naphthaleneacetates are particularly effective. The esters of the halogen-substituted phenoxy compounds are very volatile and can be used effectively for inhibiting growth by means of vapor treatments. The same substances which accelerate growth with low concentrations will inhibit growth when the concentration is great enough.

Several methods are used for inducing seedless tomatoes. The most common method is spraying the open flowers with water solutions or emulsions. The most effective concentrations for five chemicals used in treating tomatoes are as follows:

SUBSTANCE	CONCENTRATION
	mg. per liter
Indolebutyric acid	3000
β-Naphthoxyacetic acid	100
β-Naphthoxypropionic acid	50–100
β-Chlorophenoxyacetic acid	50–100
2,4-Dichlorophenoxyacetic acid	10

To apply vapors in a greenhouse, the esters are warmed over a hot plate and the air is circulated by an electric fan. For vapor treatments the esters of β-naphthoxyacetic, β-naphthoxypropionic, β-chlorophenoxyacetic, dichlorophenoxyacetic, and trichlorophenoxyacetic acids are most effective. The milligrams required per 1000 cubic feet vary with greenhouse conditions, the amount of heat applied, or other conditions, but 1–10 mg. of the dichlorophenoxyacetic acid ester, or 25–50 mg. of the β-naphthoxyacetic acid ester, would ordinarily be sufficient. Indolebutyric esters are only slightly volatile and can not be used successfully as vapors. The use of the aerosol bomb for distributing the vapors of a growth substance in a greenhouse has been successfully demonstrated (61, 62, 171), and undoubtedly will be the preferred method of treatment in the future.

In treating lawns with 2,4-dichlorophenoxyacetic acid and other similar growth substances to kill weeds, spraying the area with a mist spray is the usual procedure.

III. SUGGESTED PROBLEMS FOR INVESTIGATION

When organic growth substances first became known, and the indole compounds were the only ones of importance, some investigators of plant hormones—or auxins as they are better known—strongly suggested that the synthetic compounds had counterparts in living tissue, and that what few new growth substances might come to light would eventually be found in plants by analysis. As a matter of fact, β-indoleacetic acid is the only organic growth substance known to be synthesized by plants from among the many score and constantly increasing number of effective organic growth substances. Possibly some of these will eventually be detected in plant tissue, and undoubtedly there will be generic and specific variation in the hormones occurring in plants; but the point is that, at present, even the most confirmed "vitalist" must admit the impossibility that all growth substances can be naturally produced by plant tissue.

It is beyond the purpose of this article to suggest any new classes of organic compounds which possibly would equal or excel those already known, but inasmuch as the substituted phenoxy compounds and benzoic acids have shown such promise within the past few months, there is no reason to doubt that there are many more compounds, as yet unsynthesized, which would have increased potency.

There is need for a growth substance to induce setting of fruit without the unwanted, but usually present, formative effects. Growth substances vary greatly in their ability to set fruit and to distort the growth of leaves and stems. The ideal growth substance for the setting of fruit has not been discovered, and at present combinations of several are used because no one is entirely satisfactory.

A dependable growth substance to induce parthenocarpy in watermelon, muskmelon, and other cucurbits is not yet known. An occasional seedless watermelon has been produced, and there is no reason why some growth substance could not be effective for this purpose.

The Boyce Thompson Institute is working at present on a growth substance that can be depended on to delay the flowering of early peaches and apples. α-Naphthaleneacetic acid is used for this purpose but is not entirely effective.

No spray is yet on the market which could be used on newly purchased Christmas trees and holly wreaths to prevent the dropping of leaves.

The only really effective differential herbicides are 2,4-dichlorophenoxyacetic acid (Weedone) and 2,4,5-trichlorophenoxyacetic acid. Others equally or more effective will undoubtedly be discovered.

A plant-growth substance that will break the rest period of crab-grass seed, causing it to germinate in the fall and succumb to frost, is not beyond possibility.

A growth substance that will accelerate the growth of stems and leaves without the distortion of epinasty has unlimited uses if developed.

The field of plant hormones is still new and holds much for the future.

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THE SULFURIZATION OF UNSATURATED COMPOUNDS

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I. INTRODUCTION

The high reactivity of unsaturated compounds, as manifest by their easy addition of certain simple molecules such as halogens, has long been one of the salient characteristics of organic chemistry. The nature and products of the common additions have become well known, and the principles governing them have been established. The reaction of sulfur with saturates was also discovered early; but because its chief importance lay in the use of a complicated polymeric olefin, rubber, its mechanism has remained obscure up to the present day. Charles Goodyear discovered the vulcanization of rubber in 1839, and no work on the theory of the process was reported until the turn of the century. Since that day much labor has been expended on the structure of vulcanized rubber and, more recently, on that of factice and of the sulfurization products of olefins. It is the purpose of this review to elicit from all this research a more harmonious view of the pertinent reactions. Sulfurization of the various classes of unsaturated substances will be considered in turn.

II. SIMPLE OLEFINIC HYDROCARBONS

The first interest in the direct sulfurization of the simple olefinic hydrocarbons came with Victor Meyer's discovery of thiophene in coal-tar benzene (48). In his researches on the structure and formation of thiophene, Meyer (49, 51) showed that ethylene or acetylene and molten sulfur reacted at 300°C., forming traces of thiophene together with carbon, carbon disulfide, and hydrogen sulfide. Steinkopf and Kirchhoff (75) improved the yield of thiophene greatly by mixing the sulfur with pyrite.

The reaction of acetylene with sulfur was studied in more detail by Peel and Robinson (60), who determined that, below the boiling point of sulfur, acetylene reacts with it to give about a 5 per cent yield of thiophene, together with large amounts of carbon disulfide and hydrogen sulfide and a substance with an "unidentified garlic-like odor." At 500°C., 75 per cent of the acetylene was transformed into a brown oily product of composition 77 per cent carbon disulfide, 12 per cent thiophene, and 6 per cent thiophten. Briscoe, Peel, and Robinson (7) demonstrated that the thiophene was formed by direct reaction with the sulfur and not by a secondary reaction with carbon disulfide, for mixtures of acetylene and carbon bisulfide gave only traces of thiophene up to 350°C. and only a 12 per cent yield at 700°C. More recently Bhatt, Nargund, Kanga, and Shak (4) identified the "garlic-like odor" of Peel and Robinson as being due to thiophenol. No one seems to have speculated on the possible connection between the mechanism of the reaction and these observations that acetylene, which is known to polymerize over a wide variety of catalysts at the temperatures used (34, 79), gave all sulfuriferous products. This fact could be a clue to the course of the reaction, if studied in that light.

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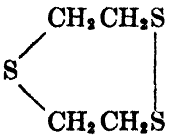
Meyer and Hohenemser (50) noted that ethylene failed to react with sulfur at 140°C. Jones and Reid (38) passed ethylene through sulfur at 325°C., to form much hydrogen sulfide and small amounts of ethyl mercaptan, ethyl sulfide, and carbon disulfide. The mercaptan and the sulfide apparently resulted from side reactions of the ethylene with the hydrogen sulfide already formed and of the mercaptan with more ethylene. The first isolation of true products from the reaction of ethylene with sulfur has been described by Westlake, Mayberry, Whitlock, West, and Haddad (88). From a reaction under pressure, using xylene as a solvent, they separated two main products, an insoluble elastomer and a xylene-soluble oil. Part of the latter was volatile. From experiments carried out to determine the structures of these products nothing could be conclusively proved, but, on the basis of the evidence obtained, they assigned either structure I or structure II to the volatile fraction and structure III to the nonvolatile fraction, and expressed the belief that the polymeric insoluble sulfide was a chain of ethylene groups linked through monosulfide and random polysulfide groups, possibly cyclized, with all sulfide linkages saturated with labile sulfur atoms. Brown (8) found in a study of this reaction that the products were strong catalysts for the reaction.



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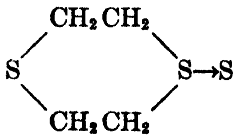

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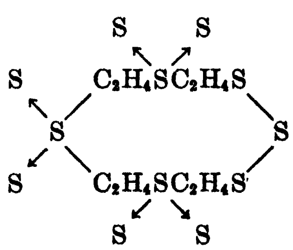
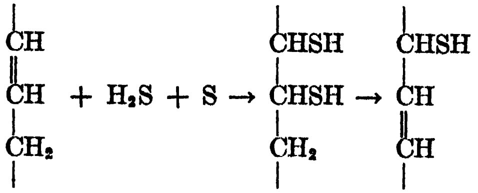


III

The sulfurization of the higher olefins has been given more attention. Friedman (26) heated hexene and sulfur under pressure and obtained a mixture of $C_6H_{12}S$, $C_{12}H_{24}S$, and $C_{18}H_{36}S$, together with an asphaltic non-volatile residue of the composition $C_{24}H_{40}S_2$. He postulated that hydrogen sulfide formed during the reaction added to the double bond to form a thioglycol, which then split hydrogen sulfide with the α-methylene group to yield an unsaturated mercaptan.

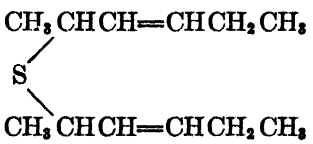


$$\begin{array}{c} | \\ CH \\ \| \\ CH \\ | \\ CH_2 \\ | \end{array} + H_2S + S \rightarrow \begin{array}{c} | \\ CHSH \\ | \\ CHSH \\ | \\ CH_2 \\ | \end{array} \rightarrow \begin{array}{c} | \\ CHSH \\ | \\ CH \\ \| \\ CH \\ | \end{array} \qquad (1)$$

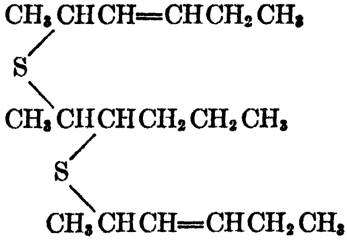
The compound $C_6H_{12}S$ he described as this mercaptan, using as a test its easy exothermic reaction with lead oxide. He then postulated an addition of this derivative to itself to form an unsaturated sulfide (equation 2). He assigned structure IV thereto

$$2C_6H_{12}S \rightarrow C_{12}H_{24}S \qquad (2)$$

and structure V to the compound $C_{18}H_{34}S_2$.



IV



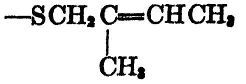
V

Friedman isolated analogous products from octene ($C_8H_{16}S$, $C_{16}H_{32}S$) and from hexadecene ($C_{16}H_{32}S$).

Quite recently an investigation has been reported by Armstrong, Little, and Doak (1), in which a number of higher olefins were sulfurized at temperatures ranging from 120°C. to 140°C. and both with and without the presence of catalysts such as rubber accelerators (2-mercaptobenzothiazole, zinc propionate, zinc oxide). Volatile and non-volatile products were obtained in varying amounts, depending on the olefin used and the conditions of the reaction (temperature, catalyst, etc.). The structure of the volatile products was investigated by ozonolysis, and it was found that they corresponded to the simplest cross-linked structures in which two olefin units were joined by one or two sulfur atoms connected to α-methylene groups. All products thus contained carbon-to-carbon cross-linking through sulfur. For example, 2-butene gave almost entirely dicrotyl sulfide (with traces of the disulfide):

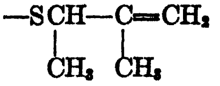
$$2CH_3CH{=}CHCH_3 + 2S \rightarrow (CH_3CH{=}CHCH_2)_2S \qquad (3)$$

Other olefins afforded mixtures of the sulfides and disulfides of allylic radicals, both symmetrical and mixed.



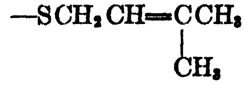
$-\text{SCH}_2\underset{\text{CH}_3}{\text{C}}{=}\text{CHCH}_3$

VI



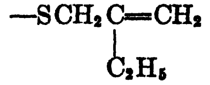
$-\text{S}\underset{\text{CH}_3}{\text{CH}}-\underset{\text{CH}_3}{\text{C}}{=}\text{CH}_2$

VII



$-\text{SCH}_2\text{CH}{=}\underset{\text{CH}_3}{\text{C}}\text{CH}_3$

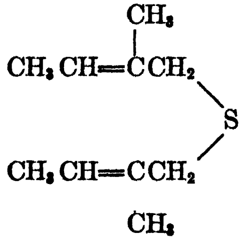
VIII



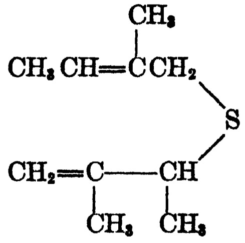
$-\text{SCH}_2\underset{\text{C}_2\text{H}_5}{\text{C}}{=}\text{CH}_2$

IX

2-Methyl-2-butene gave 70 per cent type VI radicals, 20–30 per cent type VIII, and 10 per cent type VII, and among the compounds proved to be present was bis(β-methylcrotyl) sulfide (X). 2-Methyl-1-butene formed a mixture of



X



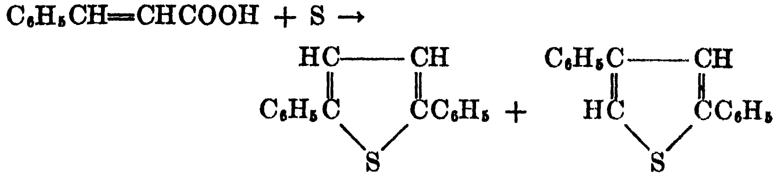
XI

radicals VI and IX connected by mono-and di-sulfide linkages.

To balance equation 3 a hydrogen sulfide molecule must be eliminated for every sulfur added. Armstrong, Little, and Doak found practically none where 5-methyl-4-nonene was heated with sulfur in the presence of a stream of nitrogen, although a methyl nonenyl disulfide was formed. The hydrogen sulfide must have been at least partly responsible for the polymers which were isolated in every case. It could also be partly responsible for the inorganic sulfide which was formed when inorganic compounding ingredients were included in the reaction mixture.

Studies have also been reported on the cycloölefins. Markownikoff and Spady (46), in a study of the constitution of naphthenes by use of the Vesterburg reaction (dehydrogenation with sulfur), had noticed the formation of high-boiling sulfur compounds in addition to the identified benzene homologs. Friedman (27) showed that dehydrogenation of cylcohexane with sulfur gave thiophenol and diphenyl sulfide as well as benzene. As sulfur does not react appreciably with benzene even at 250°C., except to form biphenyl (68), a fact which has been used to purify benzene of olefinic impurities (35, 83), this reaction may have involved partial dehydrogenation to cycloölefins and sulfurization thereof. It is more likely that the sulfurization occurred first, however, for Borsche and Lange (6) obtained cylcohexyl mercaptan from sulfur and cyclohexane, and Meyer and Hohenemser (50) found that cyclohexene and sulfur gave cyclohexyl mercaptan and cyclohexyl sulfide. The latter reaction was explained as being due to a dehydrogenation, followed by addition of the resulting hydrogen sulfide to cyclohexene. Friedman (28) sulfurized dicyclopentadiene and reported a product $C_{10}H_{12}S$, which from its formula could be an unsaturated mercaptan, but he stated that there were insufficient data to enable even a guess as to its constitution.

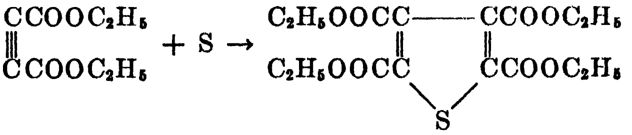
A number of substituted unsaturates have been subjected to sulfurization reactions, mostly quite drastic Thus Baumann and From (3) reacted cinnamic acid with sulfur at 210°C. for several hours, followed by 6 hr. of refluxing at 240°C., to get a mixture of diphenylthiophenes:



(4)

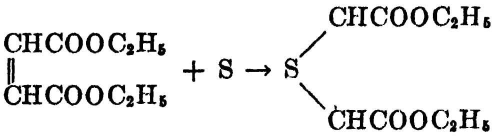
Similar treatment of styrene gave the same products. Michael (52) sulfurized styrene at 150–160°C. and reported the isolation of a compound having the composition C_8H_8S. Westlake (87) has sulfurized styrene in xylene solution and isolated as the sole product a mixture of the average composition $(C_8H_8S_3)_{2.5}$, which could be decomposed by pyrolysis to diphenylthiophene.

Michael also sulfurized acetylenedicarboxylic acid ester to form thiophenetetracarboxylic acid ester:



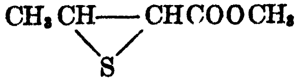
(5)

On the other hand, he reported that ethyl fumarate and sulfur gave an ethylene sulfide derivative:



(6)

This compound did not have any tendency to polymerize and could be saponified by potassium hydroxide without decomposing the sulfur ring. In view of the sensitivity to various reagents, including alkali, which Delépine (16) found ethylene sulfides of this structure to possess, and in view of the almost violent polymerization resulting therefrom, it is doubtful that the structure postulated by Michael was correct. Michael also found methyl crotonate to add one sulfur atom to give the compound $C_5H_8SO_2$, which he presumed to have the structure:

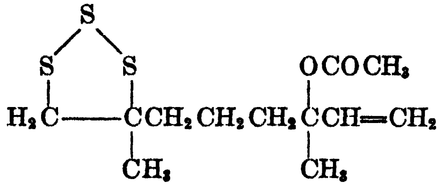


XII

The simple polyolefins have been sulfurized only at high temperatures. From butadiene and sulfur at 320–420°C. Shepard, Henne, and Midgely (70) obtained 6 per cent conversion to thiophene, while isoprene gave 47 per cent conversion to 3-methylthiophene under the same conditions. Apparently the methyl group in isoprene can affect the configuration of the molecule so as to make cyclization more probable. Westlake (87) has found no difficulty in reacting butadiene with sulfur under pressure in xylene solution. The products are red odorous oils resembling the ethylene sulfides described earlier. From the similarity in properties, a similarity in structure has been inferred but not investigated experimentally.

III. TERPENES

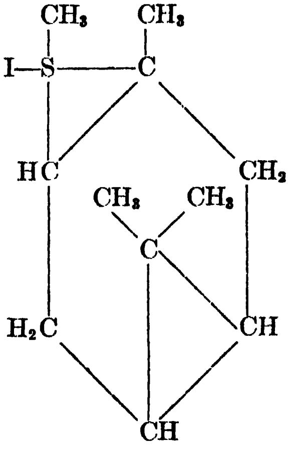
As one of the most plentiful sources of unsaturated compounds, the terpenes have been reacted with sulfur to form many useful products, such as resins, oil additives, bonding materials, and rubber substitutes. A review of such products and references to their original disclosure can be found in Ellis' *The Chemistry of Synthetic Resins* (17). The structure of the products has not received the attention it deserves. One of the first researches of relevance was that of Erdmann (18), who quite rightly pointed out that any theory regarding the sulfurization of unsaturates was dependent on the state of knowledge of the structure of sulfur. He began with the assumption that the reactive, labile, deep-red form of liquid sulfur was a short sulfur chain S_3 or thiozone, analogous to ozone, and postulated from his experimental evidence the addition of this thiozone to the unsaturate in a manner similar to ozonolysis. He reacted linaloöl and its acetate with sulfur. No reaction appeared at 150°C., but at 160°C. a lively, spontaneous exothermic reaction began with evolution of hydrogen sulfide. The product from linalyl acetate had the composition $C_{12}H_{20}O_2S_3$, which he described as the thiozonide (XIII).



XIII

He found that, with a large excess of sulfur, the product after mechanical separation of the latter was the same $C_{12}H_{20}O_2S_3$. When he used an excess of the linalyl acetate he always obtained the same product, never a lower sulfurized compound. These products were always isolated as residues, with no attempts at further purification. Erdmann further claimed that the free alcohol absorbed twice as much sulfur to form a compound which he described as a dithiozonide and which lost hydrogen sulfide on standing.

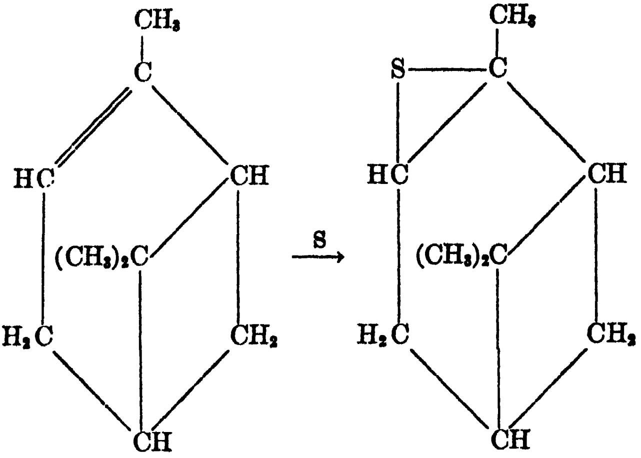
Taken by itself, Erdmann's work seems quite conclusive, except for his failure to purify his products by distillation or treatment with solvents. But no other investigator in all the fields affected by the sulfurization of unsaturated compounds has ever duplicated Erdmann's thiozonides, and some of the later work on terpenes, as well as in other sectors, appears to be quite contradictory. Budnikoff and Schilow (10, 11, 62) settled on the purification question as the cause of the differences between Erdmann's and their results. They sulfurized pinene and also Russian turpentine, which is a mixture of limonene and silvestrene, and treated the reaction products with methyl iodide to purify them, isolating a methyl iodide addition compound, apparently a sulfonium salt convertible into a sulfonium base. Their products were all compounds containing one terpene to one sulfur. For example, the product from pinene was $C_{10}H_{16}S \cdot CH_3I$, to which they gave formula XIV, although without proof.

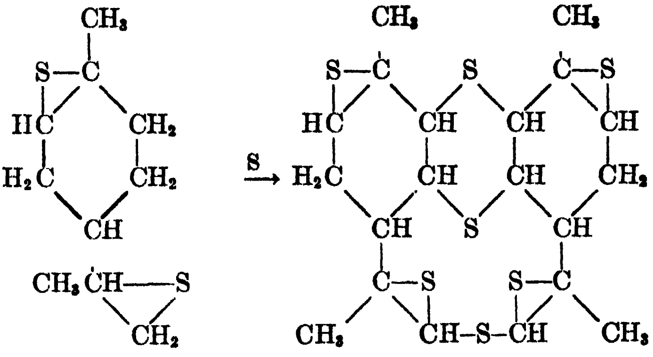


XIV

The sulfurization of American turpentine, which is principally α-pinene, has been described by Pratt (62, 63). The mixture first gave a dark liquid, which became a viscous mass and eventually a brittle substance resembling hard rubber, depending on the time and temperature of heating. By distillation and fractionation he isolated from the early liquid product without apparent decomposition a compound having the composition $C_{20}H_{24}S_5$; he postulated that it was formed by the process shown in equation 7. Analyses and molecular-weight determinations revealed that the double bonds had become saturated and that terpene residues were linked together, but no other experimental attempts to ascertain the structures were reported. The brittle product was found to have the molecular formula $C_{10}H_{12}S_4$, but no effort was made to write a structural formula for it.

A rather extensive series of researches by Nakatasuchi (55, 56, 57) on many different terpenes confirmed the results of Budnikoff that there occurred a one-to-one addition of sulfur to terpene. Thus, *d*-limonene reacted with sulfur to give a product $C_{10}H_{16}S$, to which he ascribed the structure XV, and some *p*-cymene (XVI). Many other terpenes also yielded a monosulfide.





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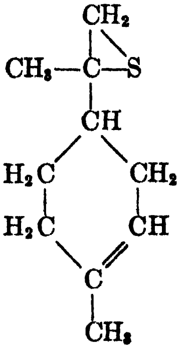
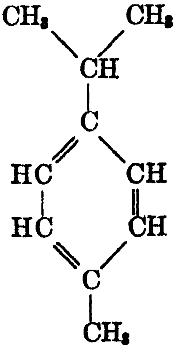
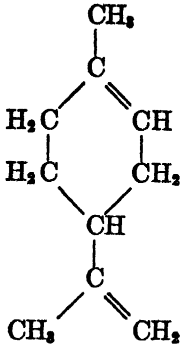


XV

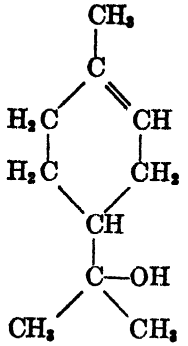


XVI

Dipentene (XVII) and α-terpineol (XVIII) gave the same $C_{10}H_{18}S$, which added one molecule of methyl iodide to furnish $C_{10}H_{18}S \cdot CH_3I$ and one bromine molecule to afford $C_{10}H_{18}SBr_2$, and was oxidized by potassium permanganate to $C_{10}H_{18}SO_2$,

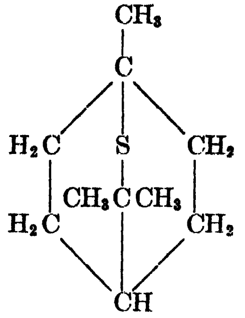


XVII



XVIII

$C_{10}H_{18}SO_3$, and $C_{10}H_{18}SO_4$. Nakatasuchi considered this compound to be a thiocineole (XIX), which is a much more likely structure than the three-membered rings favored by Pratt, Budnikoff, and even Nakatasuchi in his first paper. Probably the limonene sulfide (XV) was also a similar bicyclic compound. A structure involving substitution on each of two methylene groups alpha to a double bond would be more consistent with the observations made by other investigators on the sulfurization of the simple olefins. Certainly the possibility of such substitution will have to be investigated thoroughly before positive structures can be assigned to terpene sulfides.



XIX

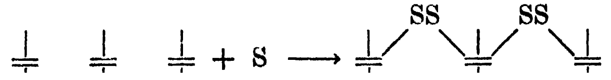
Nakatasuchi also refuted Erdmann's work by the observation that both linalyl acetate and linaloöl reacted with sulfur to give *p*-cymene, dipentene, and an unknown terpene, $C_{10}H_{16}$ or $C_{10}H_{14}$, but no sulfur compound. Unconfirmed by any other investigator, and, in fact, directly contradicted by one, Erdmann's thiozonides appear to have places on the roll of products of chemical speculation.

IV. DRYING OILS—FACTICE

Another plentiful source of unsaturated compounds is the group of glycerides of unsaturated fatty acids, usually known as the drying oils. The vulcanization of these natural products to form rubber substitutes and extenders, coatings, plasticizers, and other useful articles of commerce has been important commercially for many years. A review of their technologic aspects can be found in Ellis' *The Chemistry of Synthetic Resins* (17).

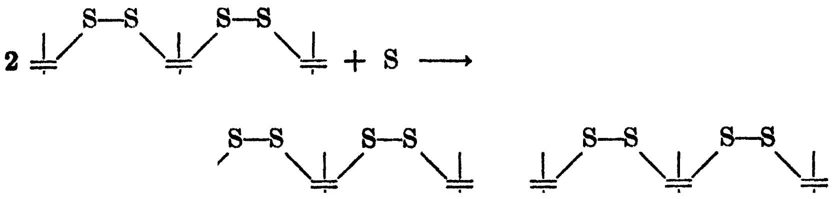
Whereas much has been published and patented concerning commercial utilization of the sulfurized drying oils, the complicated composition of the products has been relatively neglected. If sulfur is heated at vulcanizing temperatures with linseed oil, a three-stage process takes place (89). First of all, a chemical combination of the sulfur and the oil causes formation of a homogeneous mass. An acetone-insoluble polymer richer in sulfur than the remaining liquid then forms and causes gelation. Further heating transforms the gel into a solid polymer. Long, Knauss, and Small (44) showed that the second step involved a marked increase in molecular weight, indicating that the glycerides were coupling together.

Stamberger (73, 74) studied the reaction with triolein in considerable detail. He fractionated the rubbery, sulfurized triolein into three parts: acetone-soluble, acetone-insoluble but benzene-soluble, and benzene-insoluble fractions. He was able to demonstrate by molecular-weight studies and by analysis that the second fraction was about twice the molecular weight of the first and had more than twice as much sulfur. By allowing the glycerides to stand for 24 hr. in 0.5 *N* potassium hydroxide, he succeeded in saponifying them. All three fractions yielded the same tribasic acid, which analysis and molecular-weight determinations showed was a combination of three oleic acid molecules and three or four sulfur atoms. Some of the sulfur was not accounted for by this oleic acid sulfide, especially with the second and third fractions. From these data it was concluded that the first step in the reaction consisted of sulfurization and mutual linking of the three oleic acid chains, illustrated schematically by equation 8.



(8)

The formation of the second fraction was then postulated as



(9)

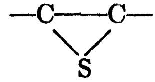
and the final step was pictured as involving continued polymerization through the glycerol residues.

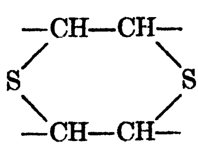
Although the work of Stamberger was conducted on a single pure glyceride, it seems highly probable that the conclusions drawn therefrom are scopeful and that natural oils combine with sulfur to form polymers whose general structures resemble those assumed for sulfurized triolein. However, the details of how the sulfur is linked in the molecule remain to be learned.

Hauser and Sze (33) recently studied the effect of sulfurization on the unsaturation and on the diene number of tung oil, which contains the triply conjugated unsaturated acid, eleostearic acid. They found that the unsaturation decreased with increasing combined sulfur but that the diene number remained constant until nearly all the sulfur which would combine had reacted. At this point one double bond had disappeared. Although the determination of diene number requires but two of the three conjugated double bonds, it is difficult to see how 1,2-addition could inhibit the further reactivity of the 5,6-position toward sulfur. They therefore concluded that the sulfur added 1,6 to the conjugated system and that steric affects rendered the remaining unsaturated system less reactive, explaining the failure of any more sulfur to combine. Hydrogen sulfide was not liberated in the early part of the reaction. The primary reaction, before secondary reactions set in, consequently appeared to be a 1,6-addition of sulfur to the conjugated system, saturating one double bond.

Hauser and Sze also investigated the rate of sulfurization of linseed oil. Here, too, the sulfur began combining at a rate of nearly two atoms for each double bond lost, but this reaction fell off rapidly. The rate of combination was greatly accelerated by the presence of zinc oxide or mercaptobenzothiazole.

It is to be noted that both the work of Nakatasuchi on terpenes (56) and that of Hauser and Sze on drying oils indicate a saturation of the double bond, while the researches of Armstrong, Little, and Doak (1) and of Friedman (26) on olefins point to a substitution on the α-carbon atom. This controversy will be met again in the following section, wherein the vulcanization of rubber is discussed.

Of interest to the general conception of the structure of factices is the work of Kaufmann, Gindsberg, Röttig, and Salchow (39) and that of Salchow (65, 66) on the preparation of ethylene sulfide derivatives of natural oils of the structure  $-\underset{\diagdown\ S\ \diagup}{C{-}{-}C}-$ by a procedure analogous to the thiocyanate method of Delépine (16) and the polymerization of these compounds to factices. By using what they called a free fat acid instead of a drying oil, they were able to get crystalline products which they considered to be dithiane derivatives:



They obtained the same compounds upon reacting sulfur chloride with the fat acid but could secure no such product from direct sulfurization. Rankoff (64), however, had reported a crystalline derivative from the action of sulfur on elaidic acid and Kaufmann believed this compound to be a dithiane-elaidic acid.

V. THE VULCANIZATION OF RUBBER

Commercially, the vulcanization of rubber forms the most important single example of the sulfurization of unsaturated compounds. From the theoretical standpoint this situation is unfortunate, for the sulfurization of a highly complex hydrocarbon such as rubber could at best be an involved process. Much more research has been carried out on the theory and mechanism of the reaction with rubber than on all the rest of the types of unsaturated compounds previously considered put together and only very recently has the importance of studying the reaction with simple molecules been recognized. Because of the complexity of the reaction and the size of the hydrocarbon, much of the earlier work was indeterminate and gave rise to many conflicting theories.

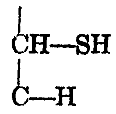
The leading controversy in the past was whether or not the change in physical properties was due to a chemical reaction and, if so, what reaction. This dispute began with the earliest researches on the theory of vulcanization and continues to the present day. Hohn (36) proposed that vulcanization consisted of adsorption of sulfur on the rubber hydrocarbon. Weber (90, 91), however, found that a part of the sulfur was not acetone-extractable and asserted that it was chemically combined. He thought he had evidence of definite compounds, but Stern (77) and Hubener (37) demonstrated that the amount of combined sulfur was proportional to the time of heating and to the initial concentration of sulfur. Ostwald (59) supported Hohn's theory mainly on the basis that Weber's data showed too low a temperature coefficient for a chemical reaction. But Spence and Young (72) determined the temperature coefficient of vulcanization to be about 2.65 per 10°C. and very recently Gerke (30) repeated the determination, confirming that it was above 2. Furthermore, Spence and Ward (71) showed that the rate of vulcanization was not dependent on the mechanical dispersion of the sulfur, a factor which would have controlled surface area in an absorption theory. It was therefore conceded that chemical combination of sulfur occurred during vulcanization. The type, degree, and method of such chemical combination remained and still are to be determined.

The early observations indicated that vulcanization was always associated with a disappearance of unsaturation. This inference led naturally to a theory that sulfur saturated the double bonds, setting up cross-linkages between hydrocarbon chains. Moreover, the vulcanization to soft rubber could be accomplished with only a small percentage of sulfur. Hard rubber, or ebonite, was formed with much more sulfur. Spence and Young (72) reported that just enough sulfur to saturate the double bonds would combine and that further heating caused no further combination. This conclusion has been somewhat disproved by Steven and Stevens (79) and by Hauser and Sze (33), who have brought out that more than the theoretical 32 per cent of sulfur will combine, owing to a substitution reaction with evolution of hydrogen sulfide. Fisher and Schubert (25) have adduced from analyses of hard rubber that, where the amount of sulfur used is theoretical (32 per cent), it adds to the unsaturation until saturation is complete, but that larger quantities of sulfur give substitution reactions. A carefully prepared ebonite had the same carbon–hydrogen ratio as rubber. This fact was confirmed by Armstrong, Little, and Doak (1), who demonstrated that no hydrogen sulfide was evolved. Wrück (94), Hauser and Sze (33), and Brown and Hauser (9, 31) have shown that the bromine or iodine number of the rubber hydrocarbon decreases in proportion to combined sulfur, a further confirmation that the vulcanization reaction involves a saturation of the double bonds. But Brown and Hauser found that, until optimum cure for soft rubber was reached, more than one sulfur per double bond was reacting.

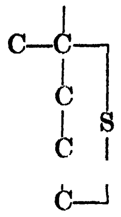
The mode of combination of sulfur in rubber has revealed itself to be just as baffling as every other phase of the complex problem. There is, for example, the belief of Kirchoff (42) that the end group on the rubber hydrocarbon is a ring which opens to give an active methylene group and that the first step of vulcanization occurs there by cross-linking of the chains. Boggs and Blake (5) concluded from a study of the heat of combustion of vulcanized rubber that Kirchoff was right, and Hauser and Sze (33) also accepted bridging at the terminal carbons as the explanation of soft rubber. The latter investigators also considered saturation of the double bonds in the middle of the chains the process which forms ebonite. Hauser and Smith (32) claimed to have obtained experimental evidence for cross-linking from x-ray examination of stretched vulcanized rubber.

Although modern investigators agree that chemical reaction between sulfur and rubber occurs, many still do not think that the phenomenon of vulcanization involves cross-linking of the hydrocarbon chain. Stevens (80) believed that vulcanization was caused by a colloidal dispersion of a rubber sulfide in the rubber. Midgley, Henne, Shepard, and Renoll (54) fractionated vulcanized rubber between benzene and alcohol and isolated a series of sulfides of the general structure RS, RS_2, RS_3, etc. They pointed out that cross-linked chains would give a series RS, R_2S, R_3S_2, etc., and regarded this observation to be evidence of no cross-linking. Williams (93) also claimed to have fractionated vulcanized rubber into portions of different sulfur content, but Kemp, Malm, Winspear, and Stirabelli (41) disproved such fractionation by a study of the diffusion of sulfur in rubber. Garvey and Forman (29) visualized vulcanication as a mechanical process involving the kinking of chains around one another, producing the effect of cross-linking with the sulfur reacting intramolecularly. Midgley, Henne, and Shepard (53) concluded from the destructive distillation of ebonite that such intramolecular addition was the case and that the thiophane rings thus formed prevented free movement of the chains, causing mechanical cross-linking.

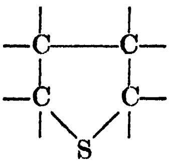
Of course the mechanism of vulcanization is not important to the subject of this paper, except as it affects knowledge of the chemical combination of the sulfur. That sulfur combines chemically is now generally conceded. The nature of the sulfide linkages in vulcanized rubber has not received the experimental attention it ought to have had. Speculation seems to have replaced research, at least in the past. Brown and Hauser (9) listed the types of linkages then believed possible, and Van Amerongen and Houvink (84) considered each of them from the standpoint of steric stability and bond strains, with the conclusion that seven were theoretically possible,—two intramolecular and five intermolecular.



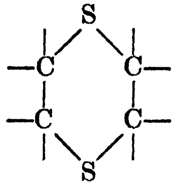
XX



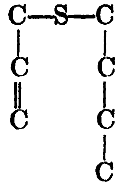
XXI



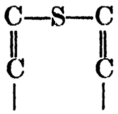
XXII



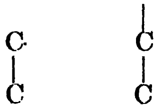
XXIII



XXIV



XXV



XXVI

XX would be formed by addition of hydrogen sulfide to a double bond, as advocated by Fisher (23), who thought that all vulcanization was caused by hydrogen sulfide generated by sulfurization of rubber or non-rubber hydrocarbon. This idea was discredited by Busse (13), who learned that hydrogen sulfide retarded the rate of vulcanization and especially interfered with accelerators, and also by Armstrong, Little, and Doak (1), who found no hydrogen sulfide evolved in the vulcanization not only of rubber but of simple olefins. Structure XXI is based on the thiophane rings favored by Midgley, Henne, and Shepard (53) from the types of thiophenes isolated by the pyrolysis of hard rubber. Because their evidence appears to be good, the occurrence of this linkage, at least in ebonite, is highly probable. XXII would be formed by simultaneous saturation of double bonds on two different chains by one sulfurization and consequent cyclization. The dithiane rings (XXIII) would result from saturation by sulfur of both ends of the two double bonds. Perhaps the ratio of between one and two sulfur atoms per double bond found by Brown and Hauser can be explained by formation of a mixture of XXII and XXIII. The type of structure represented by these two is the most probable result of any sulfurization mechanism involving direct saturation of the double bonds. Structure XXIV is the unsaturated sulfide to be expected from α-methylene attack, as postulated recently by Farmer and coworkers (19, 20, 21), which will be discussed later. It is strongly possible, as it appears to answer a number of facts. Structure XXV is far less likely, for it is difficult to see how it could be produced without substitution on double-bonded carbon itself, a reaction not backed by practical experience as is α-methylene attack. There is no evidence in favor of structure XXVI, for the only conceivable way in which it could be formed is by oxidation of a mercaptan and the saturated mercaptan would be structure XX, arguments against which have already been presented. Furthermore, there is no evidence for the presence of disulfide groups. The most probable sulfur linkages thus seem to be XXI for intramolecular and XXII, XXIII, and XXIV for intermolecular reaction.

Research on the chemical nature of the sulfur linkages in vulcanized rubber is of recent date. Meyer and Hohenemser (50) first suggested the use of methyl iodide to determine monosulfide sulfur. They reported that 80 to 90 per cent of the sulfur present was as thioether linkages. Their method was further studied by Brown and Hauser (9), who accounted for 20 to 60 per cent of the combined sulfur as thioether linkages but could not correlate this conclusion with physical properties and, as a result, belittled this method of attacking the problem. Williams (93) also doubted its value. However, Selker and Kemp (69) investigated the reaction of methyl iodide with pure organic sulfur compounds and found that each type of compound gave characteristic products in characteristic periods of time, as illustrated by equations 10 through 12:

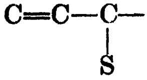
$$2RSH + 4CH_3I \xrightarrow{HgI_2} 2R_2CH_3I + 2HI \qquad (10)$$

$$RSR + CH_3I \xrightarrow{HgI_2} R_2CH_3SI \qquad (11)$$

$$(\text{unsaturated R})\ RSR + 3CH_3I \xrightarrow{HgI_2} RR + (CH_3)_3SI + I_2 \qquad (11a)$$

$$RSSR + CH_3I \xrightarrow{HgI_2} R(CH_3)_2SI + I_2 \qquad (12)$$

They reported that reactions 10 and 12 were slow, even with the mercuric iodide catalyst, while reaction 11 was quite fast. Thus they were able to determine mercaptan by titrating the hydrogen iodide. Sulfide was determined in the presence of disulfide by the weight gain of the reaction vessel in 24 hr. of contact with excess methyl iodide. Three days of contact permitted determination of disulfide. These findings were used to study the chemical binding of sulfur in vulcanized rubber. The behavior of all vulcanizates was found to resemble closely that of allyl sulfide, indicating that the group



$$\underset{\textstyle S}{\mathrm{C{=}C{-}\overset{}{C}{-}}}$$

XXVII

which is the important feature of structure XXIV, was present in large quantity. The sulfur reactable with methyl iodide appeared to be involved in linkages of this type. But in no case was all the combined sulfur in the vulcanizate removable with methyl iodide. Thiophene does not react with methyl iodide, and Selker and Kemp thought some such ring system to be the possible way of accounting for the remaining sulfur. This conclusion is interesting in view of the results of Midgley, Henne, and Shepard (53), who obtained from the pyrolysis of ebonite a distillate composed of a mixture of methyl- and ethylthiophenes. From these results they said that the thiophane rings were the principal sulfur structures formed. Probably Selker and Kemp are closer to the true picture, but it is still not entirely clear. Williams (92) has suggested that spectroscopic data might produce important evidence. The experimental difficulties involved in spectra work on a complex polymer would be in addition to the lack of spectroscopic data on sulfur linkages. Determination of such data and application to the structure of vulcanizates are certainly well-indicated lines of research. Other chemical methods of attacking the chemical linkages should also be sought.

VI. ASPHALTS AND PITCHES

The natural pitches and asphalts are sulfuriferous. Treatment of bituminous materials of various sorts with sulfur has been suggested many times as a method of preparing artificial pitches, and numerous such preparations have been patented or reported in the literature (17). The complexity of most bituminous materials, however, makes any identification of the reaction products an even more difficult problem than that encountered in vulcanized rubber. Since Lorand (45) has shown that the reaction of cracked petroleum distillates with sulfur chloride involves primarily the olefinic constituents, the same is probably true for the direct sulfurization of complex unsaturated materials.

Some of the few such products for which even the empirical composition is known were isolated by Friedmann (26, 27, 28) in his work on the sulfurization of olefins. He reported the empirical compositions of the asphaltic materials obtained as residues from the distillation of sulfur–olefin reaction mixtures. Thus, hexene and sulfur produced an asphalt $C_{24}H_{48}S_5$, octene gave $C_{24}H_{42}S$, and hexadecene yielded $C_{64}H_{48}S_5$; but their structures were not defined.

Nellensteyn and Thoenes (58) attempted to determine the part played by sulfur in the formation of natural asphalts by heating the sulfur dioxide extract of lubricating oil with sulfur at 135–300°C. They recovered most of the sulfur as hydrogen sulfide in proportion to the asphalt formed. McKinney, Mayberry, and Westlake (47) obtained products with large but undetermined percentages of combined sulfur by sulfurizing other petroleum extracts. The empirical nature of this type of sulfurization and the lack of other chemical data precluded any further discussion.

VII. MECHANISM OF THE SULFURIZATION REACTIONS

One of the complicating factors in the study of sulfurization reactions is the complex nature of sulfur itself. A halogen, for example, has a simple diatomic structure and its addition to a double bond presents no structural problem. Sulfur, on the other hand, exists in at least two allotropic solid forms and a number of reported liquid forms. It is therefore little wonder that the sulfurization of unsaturates has remained an unexplained reaction.

The possible effects of the allotropic forms of sulfur on the vulcanization of rubber have not escaped various investigators. Erdmann (18) based his theory of thiozonides on the view that the sudden change in the properties of liquid sulfur at 160°C. was attributable to the formation of thiozone, S_3. This conjecture is but part of Erdmann's speculations which were to be disproved by later investigation. Van Iterson (85) believed that the transformation of of S_λ to S_μ might govern the velocity of vulcanization. Dannenberg (15) also thought that S_μ is the allotropic form of sulfur responsible. However, Twiss (82) demonstrated that theories involving S_μ and S_π were inadequate, since S_π was found to be no better in vulcanization than S_λ. Scholz (67) deduced from the effect of accelerators in depressing the freezing point of sulfur that an equilibrium occurred in liquid sulfur according to equation 13.

$$S_8 \rightleftarrows S_4 \rightarrow S_\mu \tag{13}$$

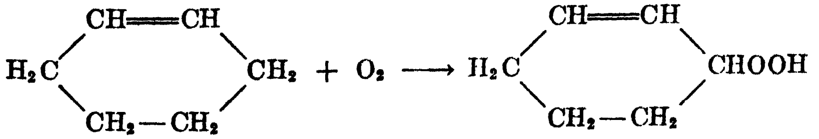
Hauser and Sze (33) also believed that an equilibrium occurred, with the formation of active forms of sulfur:

$$S_8 \rightleftarrows S_4 \rightleftarrows S_2 \rightleftarrows S_1 \tag{14}$$

However, calculations on the molecular species present in sulfur *vapor* (86), based on spectroscopic and other data (40), indicate that until well over 500°C. sulfur is principally S_8 and S_6.

The most recent publications on the structure of sulfur between 100° and 200°C. are the experimental reports of Bacon and Fanelli (2) on the viscosity of liquid sulfur and the companion theoretical studies of Powell and Eyring (61), based on Bacon and Fanelli's work. These investigators have concluded that the S_8 ring, proved by the electron-diffraction experiments of Chia-Si-Lu and Donahue (14), opens up in liquid sulfur to form S_8 chains and that the increasing concentration of those chains, as the temperature is raised, causes polymerization to long chains, forming the viscous S_μ. It is clear from this work that the conceptions of previous researchers as to the effect of the structure of sulfur on the reaction must be modified. One thing is certain, however: The structure of sulfur is intimately involved in the mechanism of sulfurization and any step in the solution of one problem is an advance in the solution of the other. The continual formation of monosulfide linkages in sulfurized products is not explained by the present accepted picture of the sulfur molecule.

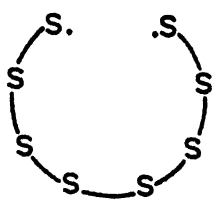
Farmer and coworkers (19, 20, 21) evolved a theory of the mechanism of sulfurization which is worth much consideration. They based it on their own and other researches on oxidation. Thus, Stephens (76) and also Farmer and Sundralingam (22) had shown that cyclohexene was oxidized to a cyclohexenyl hydroperoxide (equation 15) by oxygen. Fisher and Gray (24) found that the vulcanization of rubber with dibenzoyl peroxide occurred with the loss of unsaturation. Farmer believed that here was an instance of the reactivity of the



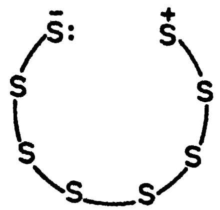
(15)

methylene groups, alpha to a double bond, for which he had gathered overwhelming evidence. Thornhill and Smith (81) reported that there was little change in the unsaturation of rubber with the first few percentages of combined sulfur, and Hauser and Brown (31) pointed out that the desirable physical properties of soft rubber were had where the combined sulfur was at the maximum obtainable without a sharp decrease in unsaturation. Farmer therefore postulated attack at the α-methylene group to form either unsaturated mercaptans or unsaturated sulfides. He felt that the later loss of unsaturation ensued from a secondary reaction, such as addition of mercaptans or hydrogen sulfide.

The normal mechanism of the addition of halogens to a double bond is ionic, but their substitution on the α-methylene group is believed to be through free radicals (21). Farmer ascribed a free-radical mechanism to the peroxidation reaction. The vulcanization of rubber has been described as a process analogous to peroxidation, involving attack on the methylene groups alpha to the double bonds. Whether the reaction is due to ions or free radicals, the opening of an S_8 ring would furnish either type of species, depending on whether the symmetrical (XXVIII) or the unsymmetrical (XXIX) splitting of the electrons occurred.



XXVIII

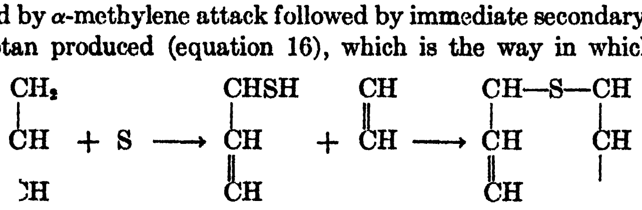


XXIX

In view of the evidence for a non-ionic mechanism quoted by Farmer, the former is the more likely.

In support of Farmer's conception of the mechanism are some of the researches previously described. Armstrong, Little, and Doak (1) isolated β,γ-unsaturated sulfides from the sulfurization of olefins. Selker and Kemp (69) showed that vulcanized rubber appeared to react like allyl sulfide toward methyl iodide. Friedmann (26) also reported obtaining unsaturated sulfides from olefins.

Opposed to the theory is much of the work on drying oils and terpenes. The investigators in these fields have almost unanimously described saturation of the double bonds rather than initial substitution. Of course the saturation could be explained by α-methylene attack followed by immediate secondary reaction of the mercaptan produced (equation 16), which is the way in which structure



$$\begin{array}{c}CH_2\\ |\\ CH\\ \\ CH\end{array} + S \longrightarrow \begin{array}{c}CHSH\\ |\\ CH\\ \|\\ CH\end{array} + \begin{array}{c}CH\\ \|\\ CH\end{array} \longrightarrow \begin{array}{ccc}CH & -S- & CH\\ | & & |\\ CH & & CH\\ \| & & |\\ CH & & \end{array} \qquad (16)$$

XXIV for vulcanized rubber could be formed. But Nakatasuchi in his work on the terpenes (55, 56, 57) continually reported the formation of ethylene sulfide rings. In view of the known instability of these rings, their formation appears doubtful and Nakatasuchi's last-reported structure, a thiocineole, appears more likely. It would be well if his work could be checked carefully. The instability of terpene structures and their ease of rearrangement would probably interfere with the obtaining of definite data, but it might be possible to reconcile a thiocineole type of structure with α-methylene attack.

Three lines of investigation appear most promising for workers interested in how sulfur reacts with the double bond. Any or all of them should give results of vital interest. First of all, the structure of liquid sulfur itself might reveal something of the manner of attack. Secondly, research on the sulfurization of olefins and of simple unsaturated compounds, such as that of Armstrong, Little, and Doak, should in the end provide the most important single collection of basic experimental data on the problem and might even be the means of studying the reaction kinetics from a theoretical or chemicophysical viewpoint. Thirdly, other methods, like that of Meyer and Hohenemser as applied by Selker and Kemp, should be developed to attack the problem of the nature and location of the sulfur linkages in the sulfurization products of the naturally occurring unsaturates. Possibly studies with infrared spectra would be one such method. Too much of the speculation in the literature is based on empirical observation or on the physical properties of the vulcanized product, which have been shown repeatedly to have no correlation with total combined sulfur. Too many secondary reactions can take place and, until they are separated from the primary reaction, no correlation can be expected.

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THE ADSORPTION WAVE[1]

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I. INTRODUCTION

The general object in the study of the adsorption wave (8, 12, 24, 25, 28, 31, 37) has been to obtain an understanding of the various factors which determine the variation in concentration of a gas effluent from a bed of adsorbent. The study of the adsorption wave consists in the consideration, from an experimental and theoretical point of view, of the distribution of gas throughout a bed, both on the adsorbent and in the air above the adsorbent. A typical distribution curve showing the concentration of gas in the air above various points in the bed of adsorbent is shown in figure 1(A). The curve for the concentrations

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which would be in equilibrium with the adsorbed gas at various points in the bed would be similar in shape but displaced slightly to the left. The term "adsorption wave" is generally applied to the movement of these distribution curves, to the right in figure 1(A), during the continuous passage of gas-laden air through the bed of adsorbent. A complete mathematical description of the wave would effect a number of important consequences. It would be possible to predict the performance of a particular bed of adsorbent, e.g., a gas-mask canister, from a minimum of experimental data and without exhaustive tests on the bed itself. It would also be possible to devise the best test procedures on small-scale beds from which to obtain the information necessary for the prediction and evaluation of the behavior of large reactors. A complete understanding of the adsorption wave would lead also to the design for the most efficient type of reactor.

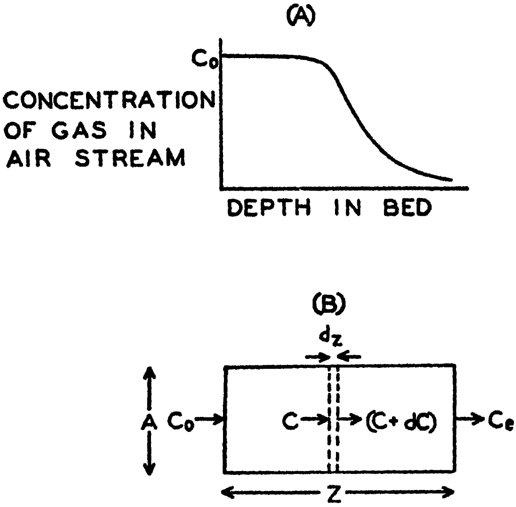

FIG. 1. Flow of gas through an adsorbent

Equal in importance to these consequences would be the elucidation of the mechanism of the adsorption process for various gases on different types of adsorbent, for such an understanding would suggest additional treatments for the improvement of the adsorbent and would also indicate when the natural limit to such improvement had been attained.

The problem of the adsorption wave has not been solved in its most general form, primarily because of the prodigious mathematical difficulties entailed (7, 8, 32, 34). In connection with this problem of correlating the performance of small-scale and large-scale reactors in chemical-engineering processes (1, 9, 11, 12, 33), the opinion has been expressed (5) that the correlation is impossible of attainment in a truly rigorous manner. Nevertheless, a number of simplified special cases of the adsorption wave have been considered and with these results as guides it has been possible to develop several semiempirical approaches to the problems of performance and mechanism of reaction.

It is generally recognized (8, 17, 20) that the removal of a gas from air by a porous adsorbent may involve one or more of the following steps: (*1*) diffusion (mass transfer) of the gas from the air to the gross surface of the granule; (*2*) diffusion of the molecules of gas into (or along the surface of) the large pores of the adsorbing particle; (*3*) adsorption of the molecules on the interior surface of the granule; (*4*) chemical reaction between the adsorbed gas and the adsorbent or adsorbed oxygen, water, or impregnant.

The relative importance of each of these four steps may vary widely with the particular conditions under which the removal is taking place. Mass transfer is influenced strongly by the flow rate of the gas stream, by the diffusion coefficient of the gas, and by the particle size of the adsorbent, but is relatively unaffected by temperature. The importance of diffusion in the pores is determined by such factors as the particle size, the structural characteristics of the pores, certain diffusional properties of the system, and the rate of reaction at the internal surface. The speed of adsorption at the interface depends on the nature and extent of the surface as well as on the activation energy for the adsorption of the particular gas under consideration. Chemical reaction is also determined by the properties of the surface, but much more specific effects will be obtained than in adsorption. Since large activation energies may be expected in steps (*3*) and (*4*), these processes will be highly sensitive to temperature.

In the general case, all four steps in the removal process may proceed with rates of approximately the same magnitude, and hence a problem of extreme mathematical difficulty is presented. On the other hand, in many situations one particular step may be much slower than the others, and hence may be considered the rate-controlling process. For a single rate-controlling process, a number of mathematical approaches have been developed. A few attempts have also been made to treat situations with more than one rate-controlling step, and for certain special circumstances, partial success has been attained.

II. Theories Predicting Effluent Concentration as a Function of Time

The ultimate aim of a mathematical analysis of the adsorption wave is an expression for the dependence of the effluent concentration on time. Even without such an expression, however, some qualitative description of the shape of an effluent–time curve can be given. Figure 2 illustrates a number of interesting cases. If the reaction on the adsorbent were instantaneous and if the adsorbent were infinitely fine-grained, none of the adsorbable gas would penetrate until some time t, at which time the adsorbent would be saturated, and then the gas would penetrate at full influent concentration. Such an adsorbent would exhibit a transmission curve such as A in figure 2. On the other hand, if the reaction is not instantaneous, a curve such as B would be exhibited. This curve would be symmetrical only for certain simple rates of adsorption. In addition to these two examples, one may encounter cases (e.g., in the removal of carbon monoxide) where the adsorbent, or its impregnant, acts as a catalyst for a reaction involving the toxic gas. As a result, the effluent–concentration curve, C, may rise very slowly; and if the catalyst remains at least partially unpoisoned, the transmission of gas may never reach the full influent value. It is also conceivable, although no such case has yet been encountered, that the rate of catalysis may be very high compared to the rate of supply of gas, and in such circumstances the transmission curve would be the time axis, that is, none of the gas would penetrate.

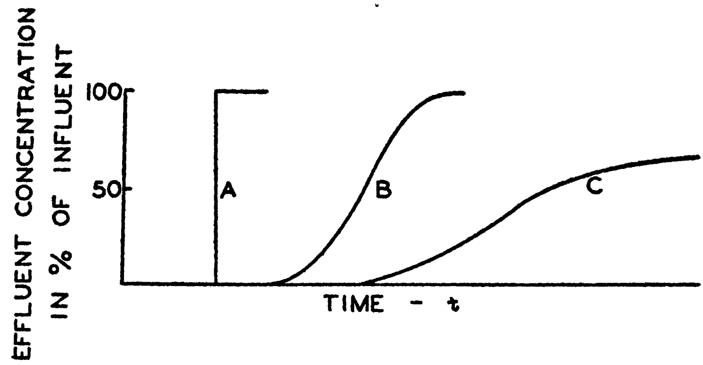

Fig. 2. Transmission of a gas by an adsorbent

A. THEORIES IN WHICH ONE STEP IS RATE-CONTROLLING

1. The general differential equation

Consider a stream of gas and air flowing through a bed of adsorbent, as is indicated in figure 1(B). Each layer of the adsorbent removes a portion of the gas from the air; hence the concentration of gas drops from an influent value of c_0 to an effluent value of c_e. A cross-section of infinitesimal thickness, dz, will reduce the concentration from c to c + dc (dc is, of course, negative). From the principle of conservation of mass it follows that

$$\text{Quantity of gas entering} = \text{quantity of gas picked up by adsorbent} + \text{quantity of gas leaving} \quad (1)$$

The quantity of gas entering the infinitesimal section of bed will be equal to the concentration, c, times the volume rate of flow, L, times the interval of flow, dt.

$$\text{Quantity of gas entering} = cL\mathrm{d}t \quad (2)$$

The amount of gas picked up by the charcoal will be given by the rate of pickup per unit volume, $\partial n/\partial t$, times the volume of the infinitesimal section of the bed (area × depth), multiplied by the interval of exposure.

$$\text{Quantity picked up by the charcoal} = \frac{\partial n}{\partial t}(A\mathrm{d}z)\mathrm{d}t \quad (3)$$

The quantity of gas leaving the section dz will obviously be given by:

$$\text{Quantity leaving} = (c + \mathrm{d}c)L\mathrm{d}t \quad (4)$$

Setting up the equality demanded by the conservation principle, one obtains

$$cL\mathrm{d}t = \frac{\partial n}{\partial t}(A\mathrm{d}z)\mathrm{d}t + (c + \mathrm{d}c)L\mathrm{d}t \tag{5}$$

which can be rearranged to give

$$-\mathrm{d}c = \frac{A}{L}\frac{\partial n}{\partial t}\mathrm{d}z \tag{6}$$

Since c is a function of the variables z and t, the total differential is (38):

$$\mathrm{d}c = \left(\frac{\partial c}{\partial z}\right)_t \mathrm{d}z + \left(\frac{\partial c}{\partial t}\right)_z \mathrm{d}t \tag{7}$$

And since

$$\partial z/\partial t = V \tag{8}$$

and

$$L = VA\alpha \tag{9}$$

where V is the linear velocity through the interstices between the particles of the adsorbent and α is the porosity (i.e., the fraction of voids per unit gross volume of bed), one obtains

$$-\left[\frac{\partial c}{\partial z}\mathrm{d}z + \frac{\partial c}{\partial t}\mathrm{d}t\right] = \frac{1}{\alpha V}\frac{\partial n}{\partial t}\mathrm{d}z \tag{10}$$

which can be rearranged to give

$$-\frac{1}{\alpha}\frac{\partial n}{\partial t} = \frac{\partial c}{\partial t} + V\frac{\partial c}{\partial z} \tag{11}$$

It is implicitly assumed in the derivation of this equation that the concentration of gas is small and that diffusion in the direction of flow is negligible.

The solution to equation 11 depends on the mathematical relation one assumes for $\partial n/\partial t$, the local rate of removal of the gas by the granules, and the particular mathematical form to be chosen depends on the mechanism of the removal process. No matter what mechanism is visualized, the local rate of removal would be dependent in general on the following variables:

(*1*) The nature of the adsorbent
(*2*) The nature of the gas to be removed
(*3*) The geometrical state of the adsorbent
(*4*) The temperature
(*5*) The local concentration of the toxic gas, as well as of other gases in the air
(*6*) The relative amount of the toxic and other gases already adsorbed by the granules
(*7*) The velocity of the gas–air stream

In all cases which have been considered, it has been assumed that the first four variables are maintained constant, but that $\partial n/\partial t$ may depend on one or more of the remaining three.

2. Diffusion as the rate-controlling step

Case a: In some cases one may encounter a gas which has no back-pressure on the adsorbent, but which nevertheless ceases to be removed by the granules when the moles of gas on the granules, n, approaches N_0, the saturation capacity of a unit gross volume of adsorbent for the gas. Under these conditions the local rate of removal would be given by the relation:

$$\frac{1}{\alpha}\frac{\partial n}{\partial t} = \frac{Fac}{\alpha\rho} \tag{12}$$

where F is the mass-transfer coefficient, a is the superficial surface per unit volume of granules, and ρ is the density of the air–gas mixture. The solution (10) of the differential equation may be resolved into two cases. For all times up to t_0 when $n = N_0$ at the entrance face, the concentration at a given point in the bed is given by the equation:

$$\frac{c}{c_0} = \mathrm{Exp}\left[-\frac{Fa}{\alpha\rho}\frac{z}{V}\right] \tag{13}$$

For times greater than t_0, the following relation holds:

$$\frac{c}{c_0} = \mathrm{Exp}\left[-\frac{Fa}{\alpha\rho}\left(\frac{z}{V} - \frac{c_0 t}{N_0}\right) - 1\right] \tag{14}$$

Case b: If a gas is adsorbed reversibly, the equation obtained for c/c_0 depends on the character of the adsorption isotherm. One of the simplest cases that has been considered is that of the linear isotherm, for which

$$c^* = bn \tag{15}$$

where c^* is the concentration of the gas in the air stream at a given point in the bed in equilibrium with the adsorbent at that point, and b is a constant. With a linear isotherm governing the back-pressure of the gas, the equation for the local rate of removal becomes (10):

$$\frac{1}{\alpha}\frac{\partial n}{\partial t} = \frac{Fa}{\alpha\rho}(c - c^*) \tag{16}$$

The solutions of the differential equations, for the boundary conditions encountered in charcoal, are well known because completely analogous equations have been encountered in the problem of heat exchange in granular beds. Analytical expressions, in terms of Bessel functions, for the solutions are cumbersome to handle, and hence the results are given best in the form of reference curves of c/c_0 as a function of the important variables. The curves worked out by Furnas (2, 13), however, are very incomplete in regions of low concentrations, the regions of great interest in work on toxic gas transmission, and consequently a semilogarithmic plot taken from a report by Hougen and Dodge (16) is given in figure 3. For values of c/c_0 below 0.01, reference should be made to the report of Drew, Spooner, and Douglas (10).

Case c: Most gases do not exhibit a linear isotherm on charcoal. A better approximation is the Langmuir isotherm, which may be expanded (10) in a power series of the form

$$c^* = \frac{Kn}{N_0} + \frac{Kn^2}{N_0^2} + \cdots \tag{17}$$

where K is a constant. Using the first two terms in equation 17 as a parabolic approximation to the isotherm, one may substitute for c^* in equation 16. The solutions of the resultant equations in terms of standard graphical procedures have been worked out and are described by Drew, Spooner, and Douglas (10).

3. Adsorption or reaction on the surface as the rate-controlling step

Case a: The earliest analysis of the adsorption wave was made by Bohart and Adams (3) on the assumption that the gas is adsorbed irreversibly and at a local rate of removal governed by the equation:

$$\frac{1}{a}\frac{\partial n}{\partial t} = k_1 c(N_0 - n) \tag{18}$$

where k_1 is a constant. A similar treatment has been carried out more recently by Hinshelwood *et al.* (6). Both groups of investigators have derived the following expression for the variation of the concentration of gas in the air stream:

$$c_0/c = 1 + (\text{Exp}\,[-k_1 c_0 t])\left(\text{Exp}\left[\frac{k_1 N_0 z}{V}\right] - 1\right) \tag{19}$$

This equation in its various forms has been used very widely to interpret and to interpolate data on the performance of various charcoals against toxic gases. Unfortunately, present indications are that there are few cases where the rate of removal of a toxic gas by charcoal as presently impregnated is governed primarily by adsorption or reaction at the surface. Diffusion, or mass transfer, seems to make some contribution to the slowness of removal of almost all gases by charcoal; hence equation 19 is not strictly applicable.

Case b: An attempt has been made by Lister (23) to consider the relations to be obtained when adsorption on the surface is the rate-controlling step but for the case where the adsorption is reversible and the adsorbed gas exerts a back-pressure. For such conditions, the equation for the local rate of adsorption becomes

$$\frac{1}{a}\frac{\partial n}{\partial t} = k_1 c(N_0 - n) - k_2 n \tag{20}$$

where k_1 and k_2 are constants.

No complete solution of the resultant differential equations has been given. Approximations have been given for the conditions obtained with fresh charcoal, but the general validity of these has been questioned (9).

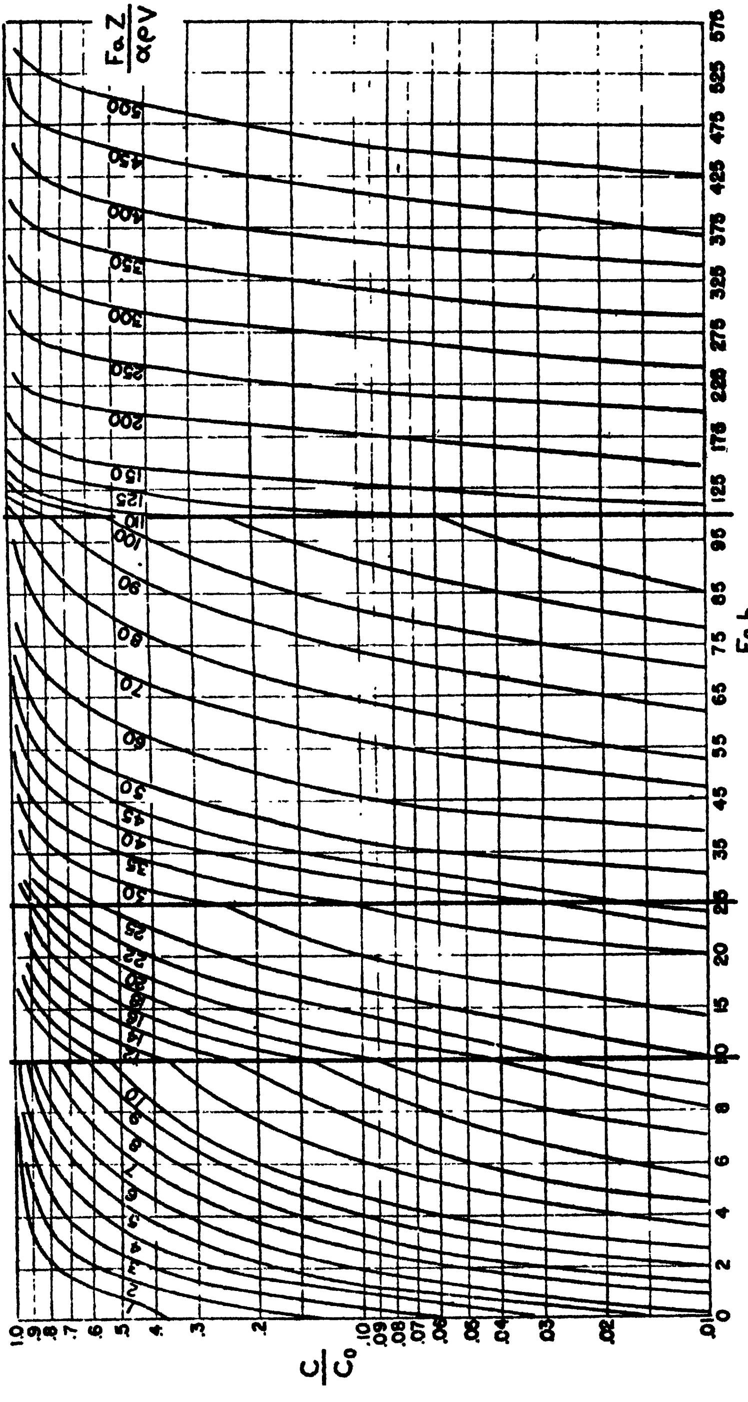

FIG. 3. Fraction of gas unremoved as a function of time and position in bed

B. THEORIES IN WHICH MORE THAN ONE STEP CONTRIBUTES TO RATE OF REMOVAL

1. Diffusion in air and deposition on surface contributing

It has been possible to construct (10) a differential equation for the local rate of removal, on the assumption that the diffusion of the toxic molecule from the air to the charcoal and the subsequent deposition process, whether chemical or adsorptive in nature, both contribute to the slowness of removal. The general equation for this process has not been solved. Nevertheless, certain special cases have been considered, but each of them reduces to one of the single-step processes discussed above and hence does not warrant further elaboration.

2. Diffusion in air and processes within the granule contributing

A very detailed consideration of the nature of the processes involved in the removal of gases by adsorbents has been made by Wicke (35). Emphasis has been given particularly to diffusion within the pores and to the various factors which influence the cross-sectional and longitudinal mixing in the intergranular spaces. Where the equilibrium adsorption of a gas follows a linear isotherm, the differential equations have been solved and have been shown to be applicable to the experimental data on the removal of carbon dioxide at 100°C. For gases with curved isotherms, however, the general solution to the differential equation has not been obtained, though certain special cases have been considered.

C. COMPARISON OF THEORIES WITH EXPERIMENT

None of the theoretical approaches gives a satisfactory correlation of the experimental data on the removal of a toxic gas by charcoal. Even with gases such as chloropicrin, where, as is shown later, mass transfer seems to be the rate-controlling step, the observed dependence of effluent concentration on time does not agree, over any appreciable range, with the curves given in figure 3. The primary cause of the deviation, for other gases as well as for chloropicrin, is the curvature of the adsorption isotherm, a condition which so far has not been incorporated, except in an approximate, empirical manner (27), into the wave equations. In addition to the curvature of the isotherm, a further difficulty that arises with most other toxic gases of interest is the combination of mass transfer and one or more of the succeeding steps in controlling the rate of removal of the gas by the adsorbent. Minor discrepancies may also arise from thermal factors. Temperature changes in the removal process, which in some cases are many tens of degrees, may raise the back-pressure of the adsorbed gas or may affect the rate of mass transfer in the carrier stream.

There exist sufficiently fundamental differences in the differential equations for the local rate of removal in the mass-transfer and surface-adsorption mechanisms so that one can determine the presence or absence of a slow diffusional step. In equation 18, based on surface adsorption as the rate-controlling step, the velocity, V, does not appear; hence in the integrated equation for c/c_0, V will enter only as z/V, as can be verified by glancing at equation 19. Similarly,

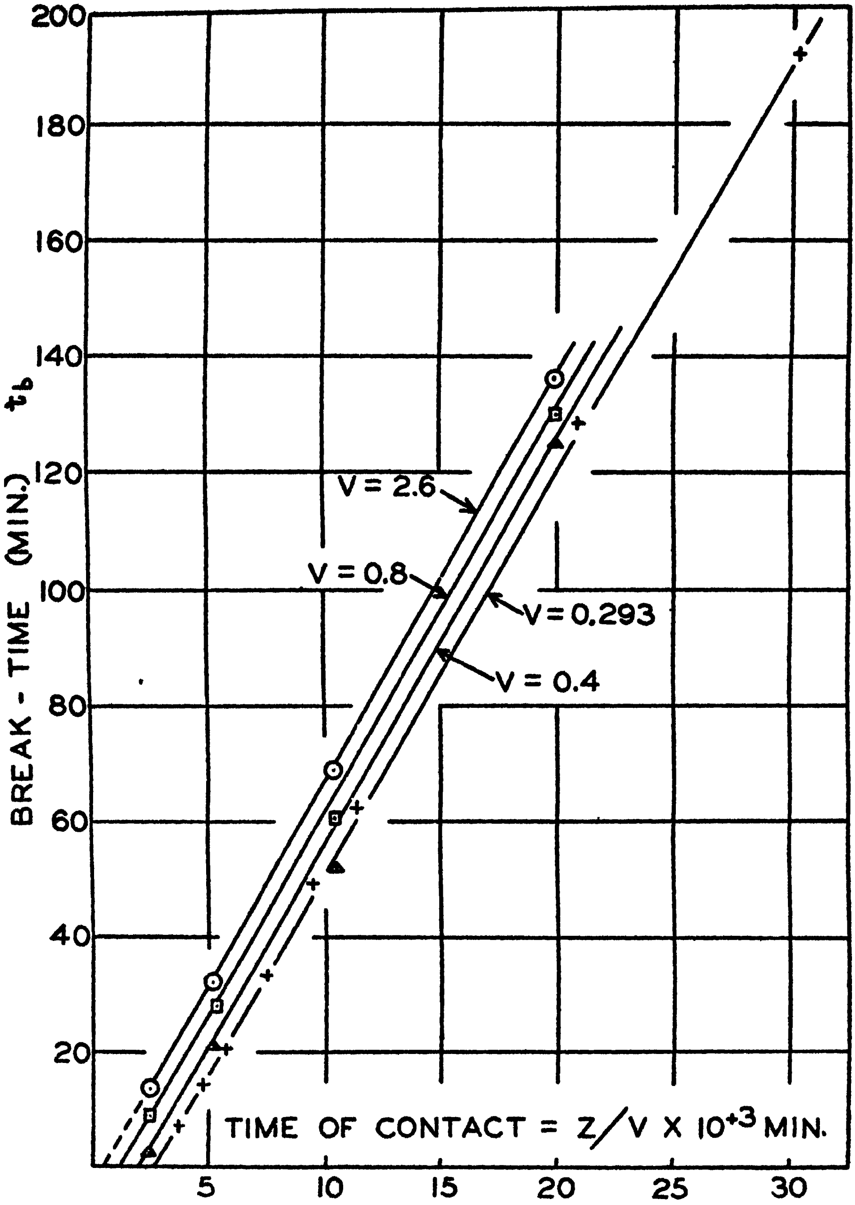

FIG. 4. Test of effect of rate of flow on local rate of removal of chloropicrin

on expanding and rearranging equation 19 to obtain an equation for t_b, the instantaneous break-time,[3] one obtains an expression in which V enters only as z/V. In contrast, when mass transfer (diffusion) is the controlling step, the velocity of flow enters the equation for the local rate of removal, inasmuch as F, the mass-transfer coefficient, depends on the rate of flow. In consequence, the instantaneous break-time depends on V as well as on z/V, and a plot of t_b *versus* z/V will give different curves for different rates of flow. (It should be emphasized that the cumulative break-time, i.e., the time in which a total quantity of gas sufficient to produce a change in some indicator has escaped from the bed, depends on V *and* z/V whether or not V enters the expression for the local rate of removal. Therefore, the cumulative break-time cannot be used to distinguish between mechanisms of removal.) Thus, a criterion has been established (9) for detecting the presence of a slow diffusional step. In figure 4, this criterion is applied to some data on chloropicrin (36). It is obvious from the graph that t_b depends on V as well as on z/V, and in consequence that diffusion contributes to the slowness of removal of chloropicrin by charcoal. Consequently, it is unlikely that the theories based on surface adsorption or surface reaction as the rate-controlling process will be applicable to any charcoal which has sufficient activity to make it useful in protection against toxic gases.

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[3] For definition see the appendix.

Unfortunately, these relationships were not realized in much of the early work and many extrapolations were made on the basis of the Bohart–Adams–Hinshelwood equation (3, 6), which is based on a surface-deposition, rate-controlling mechanism. The particularly misleading fact was the observation that in many circumstances a plot of log $[(c_0/c) - 1]$ was linear with time, a necessary condition derivable from equation 19. Unfortunately, such linearity is not a reliable test of the applicability of equation 19, for all the other mechanisms will also lead to such linear equations over wide ranges if suitable values are chosen for the constants. When constants for equation 19 are determined from plots of log $[(c_0/c) - 1]$ *versus* time, one finds that both k_1 and N_0 vary with the rate of flow of the air stream. Such behavior is completely at variance with the postulates of the mechanism and illustrates the inapplicability of the equation to the removal of gases by the usual charcoal adsorbents.

III. SEMIEMPIRICAL TREATMENTS

In the absence of a satisfactory comprehensive theory of the adsorption wave, investigators have been forced to develop semiempirical methods of treating data. Primary emphasis in work with toxic gases and charcoal has been given to equations which relate break-time to the common variables such as bed depth, rate of flow, particle size, and concentration of influent gas. With the accumulation of results from different modes of approach, it has also been possible to correlate certain relations with particular mechanisms of removal.

A. FACTORS AFFECTING BREAK-TIME

1. Nature of gas flow in charcoal

The flow of fluids through beds of granular solids is very complicated in nature for, as is quite obvious, the channels are very tortuous and non-uniform. It is impossible to fix the dimensions or number of channels, for quite frequently two streams may merge or a single stream may redistribute itself into several new paths of flow. Since sudden contractions or enlargements in intergranular spaces may exist, it is quite possible to have both streamlined and turbulent flow occurring simultaneously in different portions of a granular bed. In consequence, there is a much slower transition from conditions of laminar flow to those of turbulent flow in the passage of gas through an adsorbent bed than in the flow of fluid through pipes.

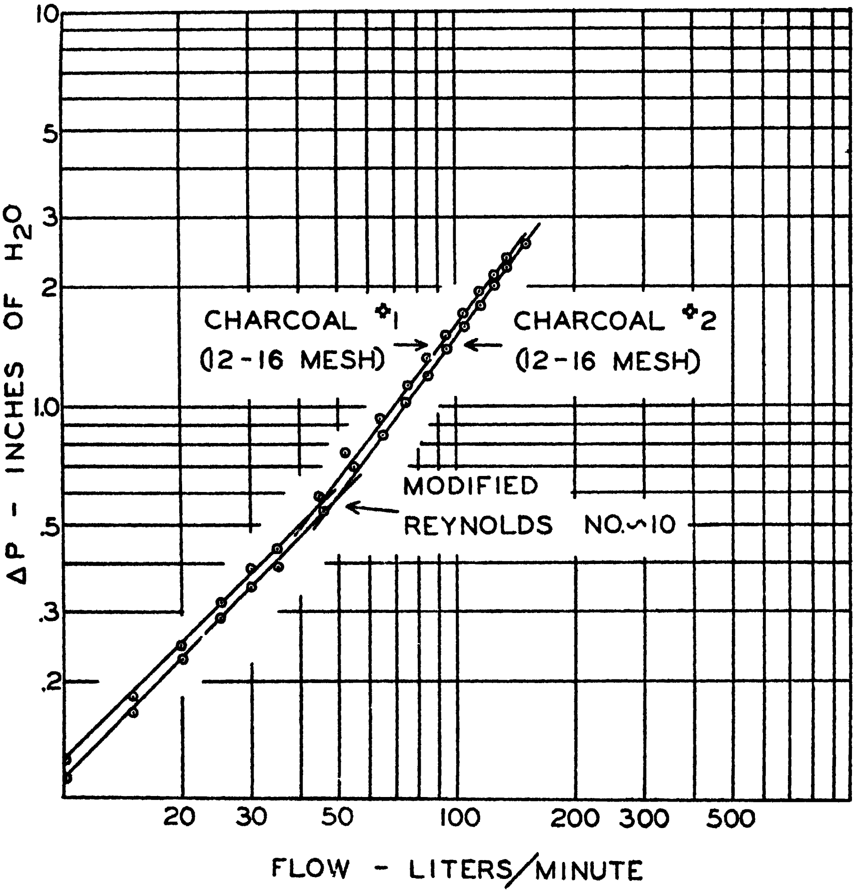

Fig. 5. Pressure-drop data

The nature of the flow of fluids is studied usually by measuring the pressure drop in the bed or pipe. Correlations are then made with the dimensionless parameter known as the Reynolds number, $D_pV\rho/\mu$. When a graph of a function of the pressure drop known as the friction factor (see 14 or 15) is plotted against the Reynolds number, two linear portions are observed, and they intersect at the so-called critical Reynolds number, a value corresponding to conditions under which laminar flow is transformed into turbulent flow.

Studies have been made of the flow of fluids through porous carbon (15), and a critical Reynolds number of about 4 has been found. Extensive work has also been carried out on the flow of gases through beds of charcoal (22). Two representative curves are shown in figure 5. From these curves and other data it has been concluded that in the charcoals investigated the critical Reynolds number is about 10. The Chemical Warfare Service laboratories (30) and English workers (19) have found a transition in the same region. Nevertheless, one cannot be certain that the same critical value will be observed with all charcoals of any possible shape. It is quite conceivable that curious shape factors may occasionally be encountered, in view of the rather arbitrary use of particle diameter, D_p, in place of pore size in the Reynolds number. In all of the work described here, however, it has been assumed that the critical region is in the neighborhood of a Reynolds number of 10.

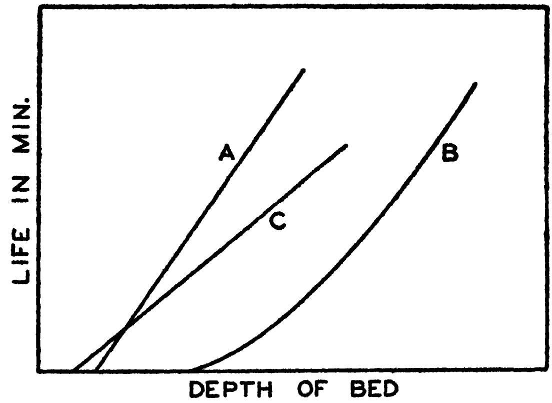

FIG. 6. Life-thickness curves

2. The effect of bed depth

The dependence of canister or tube life on the depth of charcoal has been investigated more widely than has the dependence on any other variable. The reason for such emphasis is perhaps obvious, for the amount of adsorbent necessary determines very largely the bulk of the canister. Life-thickness curves have become, therefore, the most common method of representing the performance of a charcoal. In consequence, the interpretation of performance in terms of the mechanisms of removal has revolved around the elucidation of life-thickness curves.

(a) General character of life-thickness curves

A survey of performance data shows that two types of life-thickness curves are encountered. The simplest case is a linear relation such as is shown in curve A of figure 6. Most organic gases when tested in a dry condition against dry charcoal exhibit linear life-thickness curves. In principle, a break-time test using a cumulative indicator should not show a linear relation with bed depth, at least not at small depths (27), but this lack of linearity is frequently overlooked because few tests are carried out at very small depths. Curve B exhibits a very common observation of curvature at low lives with a tendency to linearity at high break-time. Such behavior should always be encountered in cumulative tests of the break-time. It is also usually observed when tests are carried out with humidified gases and charcoal, and in some cases occurs in tests under dry conditions.

Whether or not curvature occurs, the life–thickness curve intersects the bed-depth axis at a finite value. It follows then that there exists a critical bed depth, I, below which the life is zero. This critical length will vary with the conditions of flow, concentration, mesh size, and nature of the charcoal, and it is this manifold dependence which has engaged much attention. Numerous attempts have been made to correlate these variables in some convenient analytic expression, for in small beds, as are encountered in canisters, it is the critical bed depth which primarily determines the degree of protection.

(b) The Mecklenburg equation

A very convenient expression for the linear life–thickness curve has been derived by Mecklenburg (26) from elementary considerations of conservation of mass. At the break-time a negligible portion of the toxic gas has penetrated the bed; hence one can assume that

$$\text{Weight of gas supplied} = \text{weight of gas picked up by adsorbent} \qquad (21)$$

The weight of gas supplied by the air stream will be equal to the time of flow (the break-time in minutes) times the rate of flow (in liters per minute) times the concentration (in grams per liter). In turn, the pickup by the charcoal may be *arbitrarily* considered as occurring in a certain portion of the bed instantaneously and up to the saturation value, while the remainder of the bed, defined by Mecklenburg as the "dead layer," remains completely free of gas. As was emphasized by Mecklenburg, the "dead layer" is a purely fictional concept devised merely to facilitate the derivation of the following equation and to obviate the necessity of considering in detail the distribution of gas in the bed of adsorbent. With this arbitrary division it follows that the amount picked up by the charcoal will be equal to the saturation value per unit volume times the area times the difference between the bed depth and the depth of the "dead layer," h. In algebraic terms the equality in equation 21 may be expressed as follows:

$$t_bLc_0 = N_0A(z - h) \qquad (22)$$

This equation may be rearranged readily to give an expression for the break-time:

$$t_b = \frac{N_0A}{Lc_0}(z - h) \qquad (23)$$

From this equation it is obvious that the slope of the life–thickness curve (i.e., a plot of t_b *versus* z), for a fixed rate of flow, input concentration, and bed cross-section, is a measure of the capacity (N_0) of the charcoal. For a system which obeys this equation throughout the complete life–thickness curve, the "dead layer," h, and critical bed depth, I, must be equal, so that

$$t_b = \frac{N_0 A}{L c_0} (z - I) \tag{24}$$

The great deficiency of equation 24 is that it cannot be used to extrapolate information from one set of flow or concentration conditions to another without further information on the dependence of the critical bed depth on these variables. The wave theories discussed above set certain requirements for the variation of critical bed depth, and where these theories are applicable they may be used to extend equation 24. Further details are considered in a subsequent section.

(c) Curvature due to cumulative method of test

If the break-time is defined in terms of the period necessary for a total cumulative amount of gas to penetrate the bed, it can be shown (27) that the life–thickness curve even in the simplest mechanism of removal would obey an expression of the form

$$t_c = \frac{N_0 A}{L c_0} k_3 V^{k_4} \ln \left[\frac{k_5 \operatorname{Exp}\left(\dfrac{z}{k_3 V^{k_4}}\right)}{N_0 A k_3 V^{k_4}} + 1 \right] \tag{25}$$

In general, equation 25 would not be linear; however, for large bed depths, the first term inside the brackets becomes large in comparison to the second term, 1, and the equation as a whole approaches the linear relation:

$$t_c = \frac{N_0 A z}{L c_0} + k_6 \tag{26}$$

These predictions are in agreement with the behavior observed in cumulative tests.

(d) Curvature in systems using instantaneous tests

In the testing of metal-ion-impregnated charcoals with certain inorganic gases it has always been observed that the life–thickness curves for humidified gas streams and humidified charcoal show pronounced curvature at small bed depths but approach linearity with deep beds. Curve B of figure 6 is a typical example. The increasing slope of this curve with increase in bed depth implies an increasing capacity per unit volume of adsorbent for the toxic gas. This expectation has been verified by an examination of the distribution of gas adsorbed on the bed at various time intervals. For a substance such as chloropicrin, which exhibits a linear life–thickness curve on dry charcoal, the amount of gas taken up by a unit volume of charcoal reaches a maximum which is not surpassed by increasing the time of exposure of the bed to the toxic gas. As a result, the distribution curves behave as shown in figure 7(A). In contrast, a humidified impregnated charcoal shows a continuously increasing capacity per unit volume for certain inorganic gases and in consequence exhibits a set of distribution curves such as is shown in figure 7(B). The capacity of the influent end of the bed approaches, but never quite reaches, a true saturation value, probably because a second slow reaction follows an initial rapid one. Consequently, the distribution curve is displaced upward as well as to the right toward the inside of the bed.

In a number of cases, tests carried out with dry gases on dry base charcoal have also shown curvature in their life–thickness curves. A typical example would be methyl alcohol or ethyl chloride. The curvature in all such cases, however, is less than that observed with the inorganic gases mentioned above.

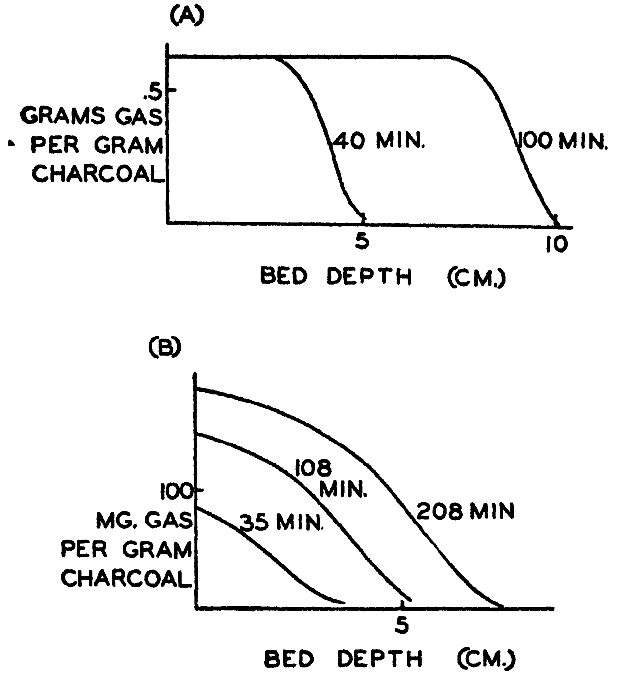

FIG. 7. Distribution of gas on adsorbent: (A) chloropicrin; (B) inorganic gas

Although no distribution curves were obtained for these dry gases, it seems likely that in these cases also some slow secondary reaction occurs in addition to the initial rapid one. For methyl alcohol it is possible that an oxidation process is being catalyzed by the charcoal. With other inert gases, and perhaps also with methyl alcohol, it seems likely that the slow reaction is a diffusion process within the pores of the granule.

3. The effects of velocity of flow, concentration, and particle size

(a) General equation for critical bed depth

It can be shown (21) from considerations similar to those discussed by Hurt (18) for the design of catalytic reactors, that if more than one step contributes to the rate of removal of a gas from the carrier stream, the critical bed depth, I, will be the sum of two terms, I_t and I_r. I_t represents the portion of the critical bed depth due to the slowness of diffusion of gas from the air stream to the surface of the charcoal, whereas I_r represents the fraction due to processes occurring within a charcoal granule. Since the critical bed depth can be thought of as the distance which the gas may penetrate the bed before its concentration is reduced to the break value, it seems reasonable to expect a certain minimum value of I, for a fixed set of conditions, which would represent the smallest penetrable depth possible even if every process in the granule were instantaneous and the rate were determined entirely by the speed with which the gas diffuses to the particle. This limiting value of I for a fixed set of conditions would be I_t. Any critical bed depth above I_t must be the contribution of the processes within the granule. That this contribution should be an additive term, rather than a multiplicative factor, has been shown in principle by Hurt (18).

The critical bed depth due to diffusion, I_t, can be expressed (20, 21) in terms of a number of familiar parameters, independent of the nature of the charcoal, but dependent on the properties of the air–gas mixture and on the granular characteristics of the bed. Considerations of dimensional analysis lead to the conclusion that, at a fixed ratio of influent to effluent concentration, I_t should be a function of the particle size of the granules and of two dimensionless parameters D_pG/μ and $\mu/\rho D_v$, the Reynolds number and Schmidt number, respectively. The specific function which has been adopted is essentially that of Gamson, Thodos, and Hougen (14)[3]:

$$I_t = \frac{2.303}{a}\left(\frac{D_pG}{\mu}\right)^{0.41}\left(\frac{\mu}{\rho D_v}\right)^{0.67}\log\left(\frac{c_0}{c_b}\right) \tag{27}$$

In the derivation of this equation it is assumed that c_0/c_b is very large. Strictly speaking, this equation should be applicable only in cases of turbulent flow, but it has been found that in the region of laminar flow in charcoal, I_t is approximated satisfactorily by equation 27. For a fixed ratio of influent to effluent concentration, the equation expresses the variation of the critical bed depth with particle size, D_p, rate of flow G, and diffusion coefficient of the gas, D_v. The factor a, the superficial surface of the granule (ignoring pore structure), depends on the particle size and on the percentage of voids in the bed. Values of a have been calculated and are tabulated by Gamson, Thodos, and Hougen (14). Where the absolute value of I_t is not desired but only the form of the equation is necessary, one can substitute the following approximate equation:

$$a = \text{constant} \times D_p^s \tag{28}$$

The power s takes into account the variation of percentage voids with particle size and generally has a value slightly less than 1.

For convenience in comparing data on critical bed depths with analogous performance data in chemical-engineering processes the following transformation is useful:

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[3] Slight changes have been suggested recently by C. R. Wilke and O. A. Hougen (Trans. Am. Inst. Chem. Engrs. 41, 445 (1945)).

$$H_t = \frac{I_t}{2.303 \log (c_0/c_b)} = \frac{1}{a}\left(\frac{D_p G}{\mu}\right)^{0.41}\left(\frac{\mu}{\rho D_v}\right)^{0.67} \tag{29}$$

H_t is called the "height of a transfer unit."

In contrast to I_t, I_r would be a complex function of the structure and nature of the charcoal and would be specific for the particular gas being removed. While it would be independent of the Reynolds number, it should (judging from consequences of equation 19) vary directly with the rate of flow of the gas–air stream, and it may be quite sensitive to temperature. Since many of these variables cannot be estimated in any general way, it is only possible to suggest the following relation for I_r (on the assumption that c_0/c_b is large and that the reaction is first order):

$$I_r = k_8 V \ln c_0/c_b \tag{30}$$

The total critical bed depth therefore should be given by the expression

$$I = I_t + I_r = \frac{1}{a}\left(\frac{D_p V \rho}{\mu}\right)^{0.41}\left(\frac{\mu}{\rho D_v}\right)^{0.67} \ln\left(\frac{c_0}{c_b}\right) + k_8 V \ln\left(\frac{c_0}{c_b}\right) \tag{31}$$

To determine the relative contributions of I_t and I_r, one may proceed in at least two ways. One approach would be to calculate I_t from equation 27 and obtain I_r by difference from the total critical bed depth. To facilitate these calculations a series of graphs has been prepared in which I_t is plotted as a function of the common variables (20). A second approach is to obtain data on I as a function of the linear velocity, V, and then to plot the data against $V^{-0.59}$. It is obvious from equation 31 that for all conditions, except flow rate, fixed, I/V may be expressed as

$$I/V = k_9 V^{-0.59} + k_{10} \tag{32}$$

where k_9 and k_{10} are constants. The intercept of the line obtained is a relative measure of I_r, and the value of the first term in equation 32 at any particular linear velocity is a relative measure of I_t.

The variation of the critical bed depth with particle size will depend on the relative importance of the two terms in equation 31, that is, on the mechanism of the removal process. I_r will be independent of particle size, whereas I_t will vary as some power of D_p, usually near 1.4. If diffusion in air and surface reaction contribute about equally, a plot of I against D_p will approach a finite limiting value as D_p approaches zero. This is illustrated by curve A in figure 8. If mass transfer alone is rate-controlling, one obtains a similar curve (B in figure 8) but with an intercept at the origin. In contrast, if the surface reaction were rate-controlling, I would be independent of granule size, as is illustrated in curve C of figure 8.

Where both terms contribute appreciably to the critical bed depth, one obtains an interesting graph in a plot of break-time *versus* particle size. For large sizes, the life is less than that for small particles, but as the granule size decreases the life rises and approaches a limiting value, corresponding to conditions where the

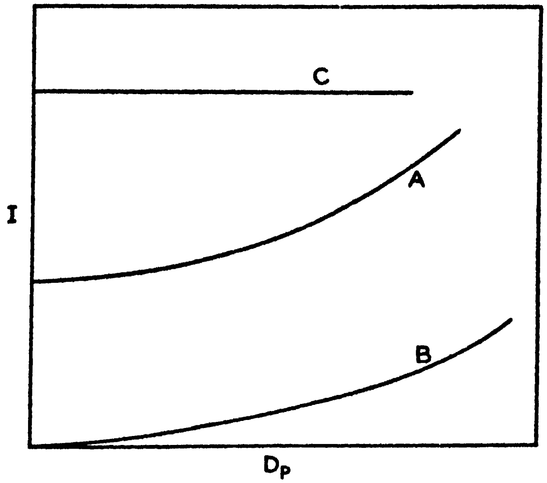

Fig. 8. Dependence of critical bed depth on particle size with different mechanisms of removal.

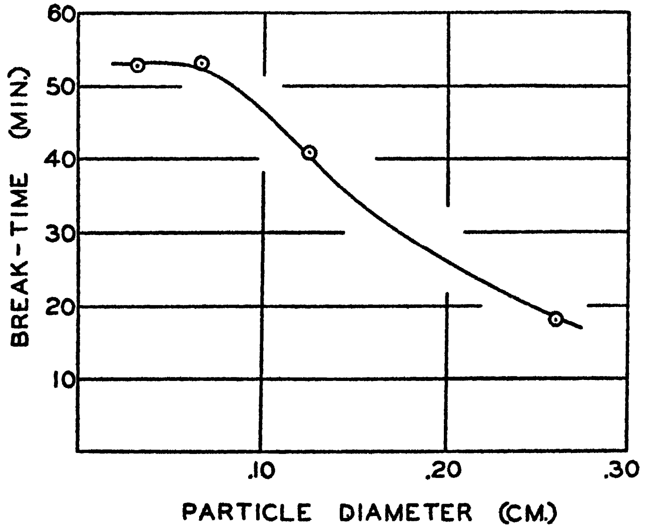

Fig. 9. Dependence of break-time on particle size; phosgene as the penetrating gas

surface reaction becomes the important factor and mass transfer has been effectively eliminated. A typical curve (29) is shown in figure 9.

The variation of the critical bed depth with velocity of flow also depends on the relative importance of the two terms in equation 31. If the slow step is a reaction in the granule, *I* will vary directly with the velocity. In contrast, if mass transfer is rate-controlling, I will vary with the 0.4 power of the velocity. Where the two processes contribute, I can usually be expressed in terms of some power of the velocity between 0.4 and 1.0, although it must be realized that such a function would be merely an approximation to the fundamental one of equation 31.

The available evidence indicates that the critical bed depth is a logarithmic function of c_0/c_b. According to equation 31, the logarithmic relation should hold for any mechanism of removal. Sufficient data on effluent concentration as a function of time are available only for a few gases, so that the predicted relation has not been tested adequately. That it does hold for chloropicrin (20) is shown in figure 10.

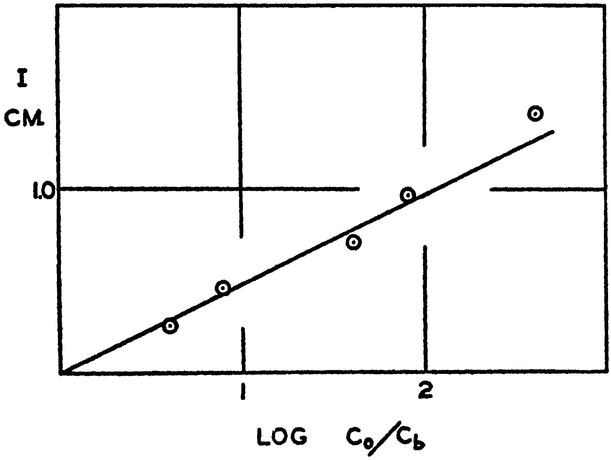

FIG. 10. Dependence of critical bed depth on ratio of influent to effluent concentration

(b) Mechanism of removal of some gases

The criteria described for estimating the relative contributions of diffusion in air and physical or chemical reactions in the charcoal to the critical bed depth have been applied to a number of gases, with the aim of elucidating the mechanism of their removal (21).

Chloropicrin is an example of a gas whose rate of removal is governed primarily by the rate of diffusion to the particle surface. In figure 11 the observed values of the critical bed depth (8, 36) are plotted as a function of the linear velocity, and for comparison the curve calculated for I_t is also shown. The observed values do not deviate significantly from the calculated curve. Such behavior indicates no appreciable contribution of any factors other than mass transfer (diffusion in air) to the removal of chloropicrin, at least not in the initial stages of the process.

In direct contrast to chloropicrin stands water, whose rate of removal seems to be governed primarily by some slow surface process. Experimental data on

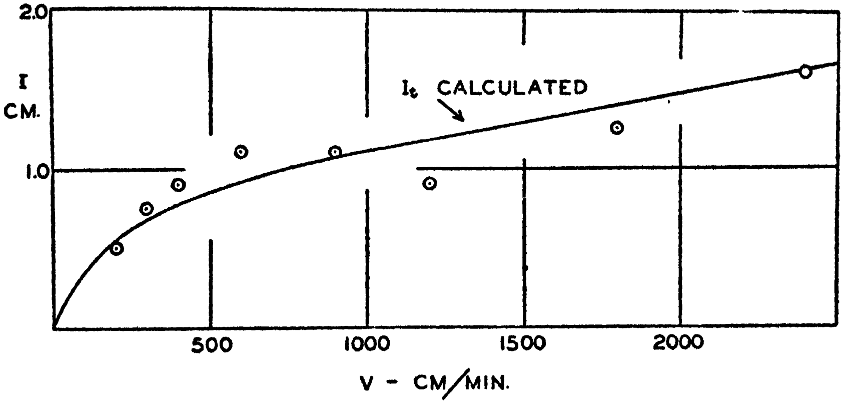

FIG. 11. Critical bed depths for chloropicrin

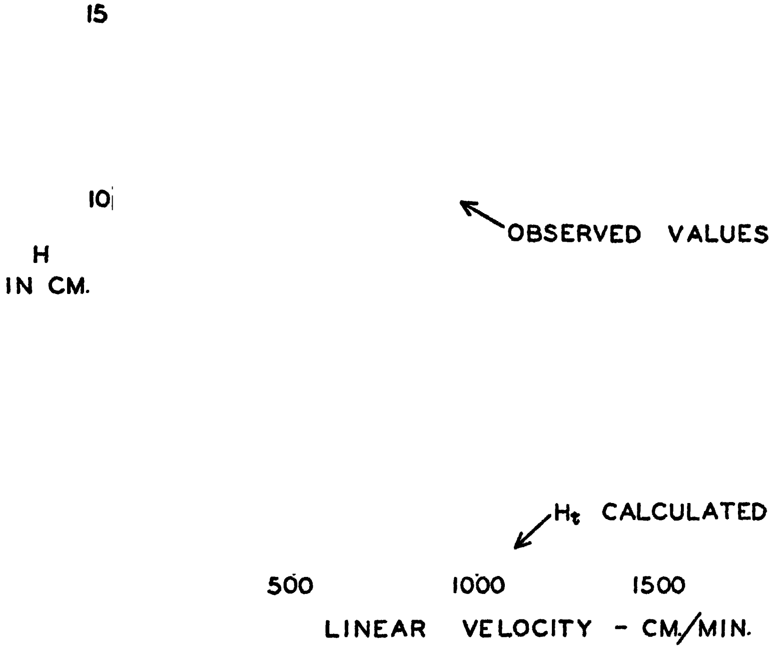

FIG. 12. Removal of water by charcoal (12–16 mesh)

the rate of removal of water (4) have been expressed in terms of a quantity which we may call H and which may be defined by the equation:

$$H = \frac{}{\ln (c_0/c_b)} \tag{33}$$

Values of H on a sample charcoal are shown in figure 12. In comparison to the values to be expected if diffusion in air were the controlling process, the observed values are very high and indicate the large contribution that is made by factors which appear within or on the granule.

Other gases are intermediate in behavior between water and chloropicrin, in that diffusion in air and surface factors contribute more nearly equally to the rate of removal of the gas.

4. Dependence of critical bed depth on adsorbent

(a) Effect of nature of adsorbent

It must be realized, of course, that the relative contribution of various steps to the rate of removal will be very sensitive to the nature of the adsorbent. This dependence is illustrated well in the case of water where different base charcoals, having different pore structures and surface complexes, can react with water with different speeds and hence influence strikingly the critical bed depth or the value of *H*. Similarly, charcoals treated with impregnants usually react more rapidly with water, apparently because of their ability to form hydrates; hence the magnitude of *H* is reduced considerably. In adsorbents such as silica gel, where the combination with water vapor at low pressures is probably due to hydrogen bonding rather than primarily to van der Waals forces, the removal reaction is extremely rapid and *H* approaches the limiting value due to diffusion in air alone. These factors are illustrated by the values of *H* listed in table 1.

TABLE 1

Dependence of H on adsorbent

ADSORBENT	*H* (4)
	cm.
Charcoal, wood base	38–64
Charcoal, coal base	20–30
Charcoal, wood base, impregnated	7–15
Silica gel	0.5–2.5

The measurement of critical bed depths for charcoals which have been subjected to various treatments is a useful method of analyzing the results obtained. For gases such as chloropicrin, at least some of the available charcoals can react so rapidly that the limiting factor in the removal of gas—the rate of diffusion to the granule—has been reached, and it is futile to attempt to improve the adsorbent any further toward these particular toxic materials. On the other hand, toward most possible toxic agents there is still sufficient room for additional treatments or impregnations which may speed up processes which occur within the granule.

(b) Effect of capacity of adsorbent

A clear statement of what is meant by "capacity" of a charcoal is not as readily available in a flow type of experiment as it is in the static case. In the latter situation, capacity refers to the amount of gas picked up by a unit weight of charcoal after sufficient time has elapsed for equilibrium to have been attained. The inapplicability of such a definition is particularly evident for a gas such as the inorganic one illustrated in figure 7(B), where the influent end of a bed has still not reached a static state even after 200 min.

The primary value of a measure of capacity is in the prediction of the dependence of life on bed depth. Consequently, it is customary to define N_0 in terms of the slope of a life–thickness curve (see equation 23). In this manner, two samples which show linear life–thickness curves can be compared reliably in their performance under a set of conditions requiring a slight extrapolation from the measured ones. It is realized of course that such a "capacity" may be far different from the final equilibrium value, even for gases removed by adsorption alone. Nevertheless, it is more useful than a definition based on a static experiment.

For small bed depths, the break-time will be determined primarily by the critical bed depth of the adsorbent, inasmuch as the critical bed depth will be a large fraction of the total bed. On the other hand, as the bed is made deeper, the critical bed depth becomes less important, whereas the capacity becomes increasingly significant and in large depths is the determining factor. These relations became evident in a comparison of the lines A and C in figure 6.

The capacity is also a useful function for estimating the maximum possible life one can obtain from a sample. By assuming a critical bed depth of zero, one can calculate the total amount of gas that could be picked up by the bed and, from the flow conditions, the maximum limit for the break-time.

B. EQUATIONS FOR CANISTER LIFE

To predict the performance of gas-mask canisters under any set of conditions other than those used in routine tests, it is necessary to have convenient analytic relations for life as a function of the common variables. This problem has not been solved satisfactorily except in a few special cases. Where the life–thickness relations show distinct curvature, no suitable analytical method has been evolved for extrapolating data. Since many tests are carried out under humid conditions, in which curvature is generally observed, this large field of testing still remains to be considered. However, in testing under dry conditions, where linear life–thickness curves are obtained, useful equations for the break-time have been developed.

1. Cases in which diffusion in air is the rate-controlling step

Under these conditions it is a simple matter to combine the Mecklenburg relation for t_b and equation 27 for I_t. The result is the expression:

$$t_b = \frac{N_0 A}{L c_0}\left[z - \frac{1}{a}\left(\frac{D_p G}{\mu}\right)^{0.41}\left(\frac{\mu}{\rho D_v}\right)^{0.67}\ln\left(\frac{c_0}{c_b}\right)\right] \qquad (34)$$

It allows the prediction of the complete break-time history for any gas whose removal is controlled by mass transfer, after the determination of one constant, N_0, the capacity of the charcoal for the particular toxic material. The diffusion coefficient, D_v, of the gas can be estimated readily from relations available in the literature, or in most cases to a sufficiently good approximation from the molecular-weight curve illustrated in figure 13. Tables of a, the superficial area, for various particle sizes and percentage of void spaces are listed by Gamson, Thodos, and Hougen (14). All other constants may be evaluated from the conditions of flow and from the dimensions of the adsorbent bed.

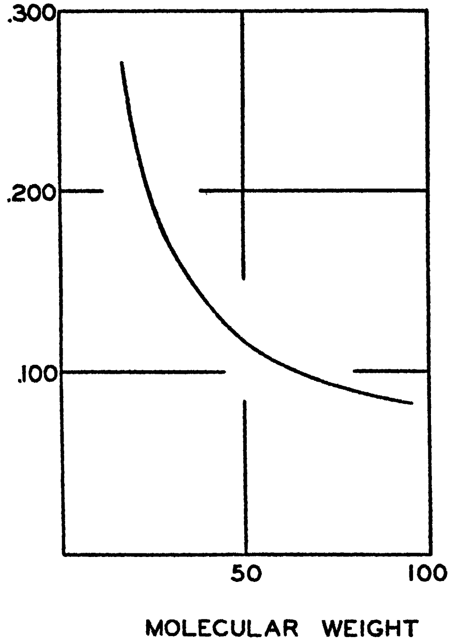

FIG. 13. Relation between diffusion coefficient and molecular weight

2. Cases in which more than one step contributes to the rate

It has been shown above that under these conditions the critical bed depth may be expressed as a sum of two terms, each of which contains the linear velocity, V, to a different power. Equation 31 for I could be inserted into the Mecklenburg relation, but the resultant expression is not as convenient for manipulation as an alternative developed by Short and Pearce (30).

It has been observed in most experiments that a plot of the critical bed depth *versus* the logarithm of the rate of flow can be approximated sufficiently well by a straight line. Because of the large errors inherent in the determination of the critical bed depth, the relation

$$I = \text{Constant} \times V^d \qquad (35)$$

where d is a constant, can be used in place of the two-term expression of equation 31. The insertion of this simple relation into the Mecklenburg equation gives:

$$t = \frac{N_0 A}{L c_0}\left[z - g\left(\frac{L_e}{A_b}\right)^d \log\left(\frac{c_0}{c_b}\right)\right] \qquad (36)$$

in which g is a constant which depends on the mesh size of the charcoal and the particular gas being removed, d is a constant determined by the test gas, A_b is the open area at the baffle at the effluent end of the canister, and L_e is the steady flow rate equivalent to the pulsating rate of flow actually used. Canister tests are made with a "breather" apparatus, designed to simulate respiratory conditions, in which the flow may vary from a high peak rate down to zero. The equivalent steady flow may be determined by measuring critical bed depths for a series of different constant flow rates and plotting I *versus* V. Then in a subsequent experiment with pulsating flow, the value of I is determined and from the reference graph a corresponding equivalent steady flow is read off. The reference curve may vary with the test gas as well as with large changes in the shape factor of the charcoal.

The use of equation 36 requires the evaluation of three constants, N_0, g, and d. The other parameters would be fixed by the conditions of flow and the geometric properties of the bed.

The equation has been applied (30) to a number of test gases (including chloropicrin and phosgene) and to a number of different charcoals and has been found to be reliable within the precision of the experimental data. Thus it affords a very convenient interpolation formula for the prediction of the performance of axial canisters.

The principles used in the derivation of equation 36 have been applied to the radial-flow canister also. The result depends, of course, on the geometrical configuration of the canister. For details reference should be made to the report of Short and Pearce (30).

IV. Conclusions

In examining the whole of the theoretical and experimental results of the work on the adsorption wave, one observes that progress has been attained in the following respects: The nature of the steps involved in the removal of a toxic gas from air by a granular adsorbent has been clearly stated. Where the rate-controlling process is a single one of these steps, it has been possible, within recognized restrictions, to develop a complete analytical expression for the adsorption wave. Where two steps contribute to the rate of removal, a complete theory is still lacking, but it has been possible to develop criteria for the evaluation of the relative importance of diffusion in air and reactions in the granule in the removal process. These criteria have been applied to a number of different gases and the mechanism of their removal by charcoal has been elucidated. From the general nature of the various equations for the adsorption wave it has been possible to develop semiempirical relations for the prediction of gas-mask canister lives under dry conditions and to predict qualitatively the effects of mesh size, flow rate, and concentration under dry or wet conditions.

The great gap in the present work is a suitable analytical treatment of results obtained under humid conditions or in other cases where non-linear life–thickness relations are obtained. Related to this is the absence of a complete treatment of the adsorption wave where many steps contribute to the rate of removal.

These failures, however, are bound very closely to the general obscurity of the structural characteristics of granular adsorbents and of the nature of catalytic reactions. As fundamental relations in these latter fields are gradually evolved, one may anticipate further progress in the treatment of the adsorption wave.

The author wishes to express his appreciation to Professor W. C. Pierce, Professor W. L. McCabe, and Captain F. G. Pearce for their advice and suggestions in the preparation of the original report from which this paper is taken. Special thanks are due to Dr. Duncan MacRae of the Chemical Warfare Service, who contributed so much to the development and clarification of the newer concepts described in this manuscript.

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VI. Appendix: Meaning of Symbols

a = superficial surface of the granule (ignoring pore structure) per unit volume of bed,
A = cross-section of adsorbent bed,
A_b = open area of the baffle at the effluent end of the gas-mask canister,
b = constant in equation for linear adsorption isotherm,
c = concentration of toxic gas in air stream at any point in bed of adsorbent,
c^* = concentration of toxic gas in air stream at any point in the bed in equilibrium with the charcoal at that point,
c_b = concentration of toxic gas in air stream chosen as the "break" value,
c_e = concentration of toxic gas in air stream at exit face of bed,
c_0 = concentration of toxic gas in air stream at entrance face of bed,
d = constant in equation for critical bed depth,
D_p = diameter of granule,
D_v = diffusion coefficient of the (toxic) gas (units of area per unit time),
Exp = notation for the exponential e; i.e., $\text{Exp}(x) = e^x$,
F = mass-transfer coefficient,
g = constant in equation for gas-mask canister life,
G = mass velocity, i.e., weight per unit time per unit cross-section of bed,
h = depth of the "dead layer,"
H = height of a removal unit $= I/(\ln c_0/c_b)$,
H_t = height of a transfer unit $= I_t/(\ln c_0/c_b)$,
I = critical bed depth, i.e., the actual intercept of a life–thickness curve on the thickness axis,
I_r = fraction of critical bed depth due to slowness of processes occurring within a charcoal granule,
I_t = fraction of critical bed depth due to slowness of diffusion of gas from air stream to the surface of the charcoal,
k_1 = constant in rate equation,
k_2 = constant in rate equation,
k_3 = constant in equation for t_c,
k_4 = constant in equation for t_c,
k_5 = constant in equation for t_c,
k_6 = constant in equation for t_c,
k_7 = constant in equation for critical bed depth,
k_8 = constant in equation for critical bed depth,
K = constant in the expanded form of the Langmuir isotherm,

L = rate of flow in liters per minute,
L_e = rate of steady flow equivalent to rate of pulsating flow,
n = moles of toxic gas on or in the granules contained in a unit volume of bed,
N_0 = saturation capacity of a unit gross volume of adsorbent for the (toxic) gas,
s = constant in equation for superficial area,
t = time,
t_b = "instantaneous" break-time, i.e., the time at which the effluent concentration reaches a value specified as the break concentration,
t_c = "cumulative" break-time, i.e., the time necessary for a given total amount of gas to penetrate the adsorbent,
V = linear velocity through the interstices between the particles of the adsorbent = $G/\alpha\rho$,
z = distance from the entrance face of the bed,
α = porosity, i.e., the volume of intergranular voids per unit gross volume of bed,
μ = viscosity of gas–air stream,
ρ = density of gas–air stream.

THE SULFENIC ACIDS AND THEIR DERIVATIVES

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I. INTRODUCTION

The sulfenic acids are generally designated as organic compounds of bivalent sulfur which correspond to the formula RSOH.[2] Although there is but one instance of the isolation of an acid of this type,—namely, 1-anthraquinonesulfenic acid,—substances which may be conveniently classified as derivatives of these acids are well known. The first section of this review will concern itself chiefly with the sulfenic acids as such. Subsequent sections will consider the sulfenyl halides (RSX), the sulfenyl thiocyanates (RSSCN), the sulfenamides ($RSNR_2$), the alkyl and aryl sulfenates (RSOR′), and the sulfenic anhydrides (RSOSR). A concise discussion of this subject has been presented previously by Connor (21). From a geometric viewpoint, it is possible to regard certain other substances, for example, the organic thiocyanates or the isothiazoles, as derivatives of sulfenic acids. Compounds such as the latter, however, will be included in this review only insofar as they may occur as products in the reactions of substances under primary consideration.

Of the inorganic oxygen acids of sulfur, only those in which the sulfur atom displays its maximum valence of six can be isolated in the free state. In contrast to sulfuric acid, sulfurous acid and sulfoxylic acid (HOSOH) have not as yet been isolated (27, 36). In considering the organic oxygen acids of sulfur, a similar relation between the oxidation state of the sulfur atom and the ability of the corresponding acids to exist as such is to be found among sulfonic, sulfinic, and sulfenic acids. It is generally recognized that the sulfinic acids are decidedly more subject to decomposition than are the corresponding sulfonic acids (2, 35, 78). The still lesser tendency of the sulfenic acids to remain structurally intact is implied by the circumstance that only one such acid has been reported, and is emphasized by the fact that the hydrolytic reactions of various sulfenic acid derivatives cannot be correctly formulated by a simple metathetical exchange as shown in equation 1.

$$RSX + HOH \rightarrow RSOH + HX \qquad (1)$$

---

[2] English authors have used the term "sulphoxylic acids" (55, 82); the German designation is "Sulfensäure."

Such reactions are reported, instead, to give rise to a variety of products, including sulfinic acids, disulfides, sulfenic anhydrides, and thiolsulfonic esters.[3] Specific examples of such changes will be considered in appropriate places throughout this paper.

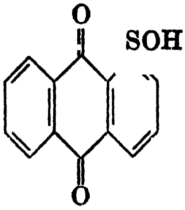
II. THE SULFENIC ACIDS

A. EARLY WORK OF FRIES

In 1912, Fries (30) reported the synthesis of 1-anthraquinonesulfenic acid (IV) by the steps shown below (R = 1-anthraquinonyl).

$$\underset{}{\mathrm{RCl}} \xrightarrow{\mathrm{Na_2S_2}} \underset{\mathrm{A}}{\mathrm{RSSR}} \xrightarrow{\mathrm{Br_2}} \underset{\mathrm{B}}{\mathrm{RSBr}} \xrightarrow{\mathrm{CH_3OH}} \underset{\mathrm{C}}{\mathrm{RSOCH_3}}$$

$$\mathrm{C} \xrightarrow{\mathrm{KOH}} \underset{\mathrm{D}}{\mathrm{RSOK}} \rightarrow \qquad (2)$$



IV

Although it would seem that 1-anthraquinonesulfenic acid could be obtained directly from the sulfenyl bromide (B), this was not found to be the case. If the latter was treated with aqueous sodium hydroxide, instead of the expected salt there was obtained 1-anthraquinonyl disulfide (A), and by acidification of the hydrolysate, 1-anthraquinonesulfinic acid. With alcoholic solutions of sodium or potassium hydroxide, the formation of the disulfide (A) and of the sulfinate salt occurred more rapidly, and, simultaneously, the characteristic color associated with the salts of 1-anthraquinonesulfenic acid was observed. In the reaction of 1-anthraquinonesulfenyl bromide with sulfuric acid, there was also obtained a mixture of products wihich consisted principally of the disulfide (A) and 1-anthraquinonesulfenic acid. 1-Anthraquinonesulfenyl bromide, how-

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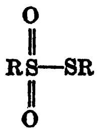
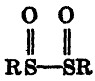
[3] There is some question in the literature as to whether the products obtained are thiolsulfonic esters (I), disulfoxides (II), or possibly mixed anhydrides of sulfinic and sulfenic acids (III).



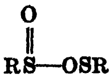
$$\mathrm{R}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\underset{\underset{\displaystyle \mathrm{O}}{\|}}{\mathrm{S}}}\text{—SR}$$

I



$$\mathrm{R}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{S}}\text{—}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{S}}\mathrm{R}$$

II

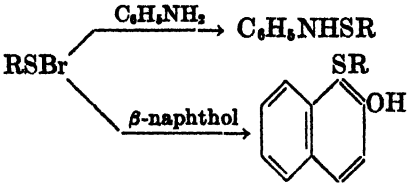


$$\mathrm{R}\overset{\overset{\displaystyle \mathrm{O}}{\|}}{\mathrm{S}}\text{—OSR}$$

III

From the studies concerned with these substances (21, 35, 43, 44, 51, 52, 71, 80, 81), it may be concluded that the thiolsulfonic ester structure is in best agreement with the experimental evidence. When these products are referred to in a general sense, in this paper, they will be designated as thiolsulfonic esters. In specific instances, however, the name used by the author whose work is cited will be employed.

ever, was found to resemble other aromatic sulfenyl halides in its reactions with ammonia, amines, and phenols. Thus, with aniline (32) and with β-naphthol (30), the products shown in equations 3 and 4 were obtained (R = 1-anthraquinonyl).



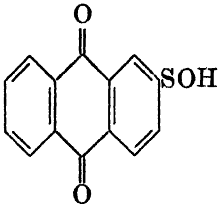
(3)

(4)

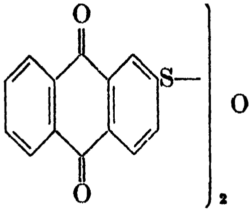
1-Anthraquinonesulfenyl bromide was converted to methyl 1-anthraquinonesulfenate (C) by reaction with boiling methanol. When the methylsulfenate was heated with 33 per cent potassium hydroxide solution for a few minutes, the potassium salt (D) was precipitated. By acidification, free 1-anthraquinonesulfenic acid (IV) was obtained in the form of bright red crystals, which could be recrystallized from benzene if certain precautions were taken. When subjected to heat, the free acid began to lose water at 100°C., but the sample did not melt completely even at 300°C. The main product of thermal decomposition was the sulfenic anhydride (see table 5), with some accompanying disulfide and "disulfoxide." By reaction with hydrogen chloride and hydrogen bromide, the sulfenic acid was reconverted to the known 1-anthraquinonesulfenyl chloride and the original sulfenyl bromide (B). In contrast to these results with hydrogen chloride and hydrogen bromide, it was later reported that the action of hydrogen iodide on 1-anthraquinonesulfenic acid resulted in the formation of the disulfide (A) rather than of 1-anthraquinonesulfenyl iodide (31). Reaction of the free acid with sodium sulfide gave 1-mercaptoanthraquinone, whereas with β-naphthol, the sulfide shown in equation 4 was obtained. Free 1-anthraquinonesulfenic acid displayed distinctly acid properties. It dissolved in aqueous or alcoholic solutions of sodium or potassium hydroxide, sodium carbonate, or ammonia to form solutions of characteristic color. When isolated, the salt crystals appeared black, with a metallic green surface luster. The sodium and potassium salts dissolved in absolute alcohol with development of a brilliant green color, while aqueous solutions were of pure blue tint. These salts were easily soluble in water, but were extensively hydrolyzed. The lead and barium salts, however, were only slightly soluble in water. If air was excluded, solutions of the acid (IV) in alcoholic potassium hydroxide remained unaltered; but if air was admitted, or more quickly with potassium ferricyanide, oxidation to the sulfinate occurred. An interesting difference between the salts and the free sulfenic acid was noted. In reactions of the free acid with methyl sulfate or methyl alcohol, methyl 1-anthraquinonesulfenate (C) was obtained. By treatment of the sodium or potassium salts of IV with methyl sulfate, however, the distinctly different methyl 1-anthraquinonyl sulfoxide was obtained exclusively. This difference between 1-anthraquinonesulfenic acid and its salts was also observed in the reactions of these substances with ethyl sulfate and ethyl alcohol (32). In this behavior, the salts of 1-anthraquinonesulfenic acid resemble those of sulfinic acids, for the latter also give sulfones, rather than sulfinic esters, when treated with alkyl halides and alkyl sulfates (79, 86), as well as with certain heterocyclic halogen derivatives, such as 5-amino-8-chloroquinoline (4). Probably on the basis of this contrasting behavior of 1-anthraquinonesulfenic acid and its salts, as well as to facilitate his understanding of the various products obtained by hydrolysis of 1-anthraquinonesulfenyl bromide, Fries suggested that the acid may exist in a "pseudo" structure, $R\overset{H}{S}O$. Similar considerations, with less experimental basis, were also made some years earlier by Gutmann in a discussion of the probable structure of ethanesulfenic acid (46).

B. LATER WORK OF FRIES AND COWORKERS

A portion of the experimental work of Fries was described above to show that this investigator had reasonable basis for reporting the isolation of 1-anthraquinonesulfenic acid. In 1919, Fries and Schürmann (32) reported their attempts to isolate 2-anthraquinonesulfenic acid. The conversion of 2-anthraquinonesulfenyl chloride to the free sulfenic acid (V) could not be effected. Instead, there was obtained its anhydride (VI). The latter dissolved in alcoholic sodium hydroxide to form a red solution, from which the original anhydride (VI) was reprecipitated by acidification. The development of a characteristic color during solution of VI in alcoholic sodium or potassium hydroxide was in accord with experiments of Zincke concerning sulfenic anhydrides, such as those corresponding to the acids VII, VIII, and IX shown below (106, 108, 109, 113, 114). Following the suggestion of Zincke, it was considered that the formation of the salts of 2-anthraquinonesulfenic acid was the cause of the color. However, all attempts to isolate 2-anthraquinonesulfenic acid (V), by the same methods as were effective for 1-anthraquinonesulfenic acid, were not successful.



V



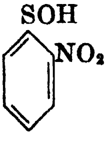
VI

Additional investigations were carried out by Fries and Schürmann (32, 33) with the intent to obtain other sulfenic acids in the anthraquinone series. By methods similar to those described above, they sought to prepare 4-hydroxy-1-anthraquinonesulfenic acid, 4-ethoxy-1-anthraquinonesulfenic acid, and 4-amino-1-anthraquinonesulfenic acid. In the attempted syntheses of these compounds, difficulties were encountered in preparing the sulfenyl halides required as starting materials. In the reactions of the 4-hydroxy- and 4-methoxy-1-anthraquinonyl disulfides with chlorine, under conditions similar to those previously used to prepare 1-anthraquinonesulfenyl chloride, the products obtained were the 1-anthraquinonesulfonyl chlorides, rather than the desired sulfenyl chlorides.

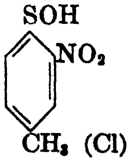
With 4-amino-1-anthraquinonyl disulfide, there was formed 3-chloro-4-amino-1-anthraquinonesulfonyl chloride. The preparation of the sulfenyl bromides from the 4-hydroxy- and 4-ethoxy-1-anthraquinonyl disulfides could not be achieved, because bromine failed to effect the cleavage of the disulfide linkage in these compounds. By reaction of 4-amino-1-anthraquinonyl disulfide with bromine, however, there was obtained the hydrobromide of 4-amino-1-anthraquinonesulfenyl bromide (33). The identity of the latter was established by analysis and the nature of its typical reactions. It dissolved in alcoholic solutions of sodium or potassium hydroxide to give deep green solutions of the sodium or potassium salts of 4-amino-1-anthraquinonesulfenic acid. These salts behaved in the same manner as those of 1-anthraquinonesulfenic acid: with hydrogen bromide, in acetic acid solution, they yielded the original sulfenyl bromide; by oxidation with air, and acidification, the corresponding sulfinic acid was obtained; and by the action of methyl sulfate, methyl 4-amino-1-anthraquinonyl sulfoxide was formed. Free 4-amino-1-anthraquinonesulfenic acid, however, could not be obtained in a condition suitable for analysis. By hydrolysis of the salts in acid solution there was formed a red precipitate which, "after short standing," could not be reconverted to the original salts of the sulfenic acid. The analysis of the hydrolysate showed it to consist mainly of the sulfinic acid and the disulfide. These changes had also been observed with 1-anthraquinonesulfenic acid. With the latter compound, however, they occurred only when a glacial acetic acid solution of the sulfenic acid was boiled, whereas with the product presumed to be 4-amino-1-anthraquinonesulfenic acid, the decomposition took place instantaneously.

C. OTHER ATTEMPTS TO ISOLATE SULFENIC ACIDS

Attempts to isolate free sulfenic acids in other series have been attended with even less success than in the anthraquinone series. Those of Zincke and coworkers (106, 108, 109, 113, 114) to obtain free sulfenic acids, such as VII, VIII, IX, and X, from the corresponding sulfenyl chlorides, led invariably to the formation of products such as the corresponding sulfinic acids, disulfides, sulfenic anhydrides, "disulfoxides," and sulfonyl chlorides, but the free sulfenic acids or their salts could not be isolated. Such repeated failures seem to have discouraged other investigators from pursuing studies whose central aim would be the isolation of free sulfenic acids. There are, however, the records of a number of investigators who were not primarily interested in the isolation of sulfenic acids, but who found it convenient to assume the formation of these acids as intermediates in various reactions (34, 35, 45, 46, 50, 55, 64, 71, 82, 89). As a single



VII



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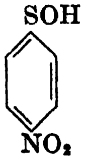
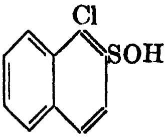


IX



X

example of several similar postulations, Lecher (64) proposed that benzenesulfenic acid (C_6H_5SOH) was the first product of the hydrolysis of benzenesulfenyl chloride to benzenesulfinic acid and phenyl disulfide (compare the hydrolysis of benzeneselenenyl bromide, page 278). Hinsberg (50, 51) and Fromm (35) postulated sulfenic acids as primary products in the decomposition of sulfinic acids:

$$2RSO_2H \rightarrow RSOH + RSO_3H \qquad (5)$$

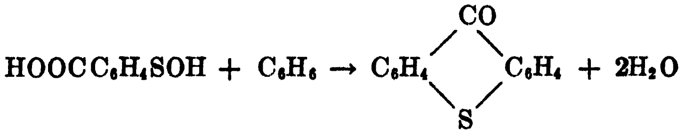
On the basis of the sulfenic acids as intermediates, these authors accounted for the formation of the products found in the decomposition mixtures of sulfinic acids, as well as for such products as amino sulfides or hydroxy sulfides which are obtained in the reactions of the sulfinic acids with aromatic amines or phenols (see equations 11). Additional examples of the postulation of sulfenic acids as intermediates, which may be briefly mentioned, are those of Prescott and Smiles (82) and of Schöberl (89), who considered that sulfenic acids and mercaptans were obtained in the hydrolytic scissions of disulfides.

$$RSSR + HOH \leftrightarrows RSH + RSOH \qquad (6)$$

Davis and Smiles (23) and Marsden and Smiles (68) considered that there was no satisfactory alternative to the assumption of the intermediate formation of sulfenic acids in the preparation of thioxanthone and substituted thioxanthones, as shown in equations 7, 8, and 9.

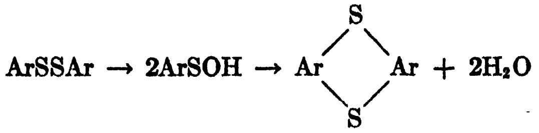
$$HOOCC_6H_4SH + H_2SO_4 \rightarrow HOOCC_6H_4SOH + H_2SO_3 \qquad (7)$$

$$HOOCC_6H_4SOH + HSC_6H_4COOH \leftrightarrows (HOOCC_6H_4S)_2 + H_2O \qquad (8)$$



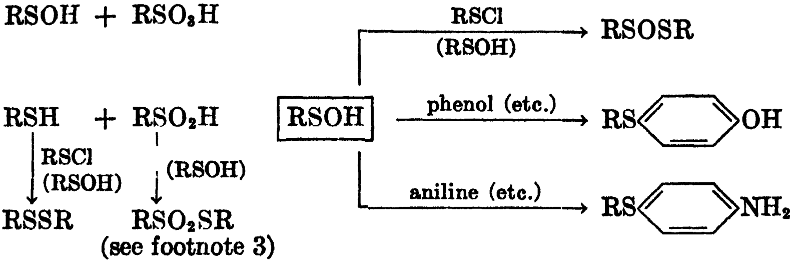
$$HOOCC_6H_4SOH + C_6H_6 \rightarrow C_6H_4\begin{matrix}CO\\ \diagup\quad\diagdown\\ \diagdown\quad\diagup\\ S\end{matrix}C_6H_4 + 2H_2O \qquad (9)$$

These authors have presented evidence for the reversibility of the hydrolytic scissions of the disulfides (equations 6 and 8). Another interesting example of the postulation of intermediate sulfenic acids is found in the interpretation of the formation of thianthrenes from disulfides (55).



$$ArSSAr \rightarrow 2ArSOH \rightarrow Ar\begin{matrix}S\\ \diagup\quad\diagdown\\ \diagdown\quad\diagup\\ S\end{matrix}Ar + 2H_2O \qquad (10)$$

Gutmann (45, 46) considered that ethanesulfenic acid (C_2H_5SOH) was formed as an intermediate product when sodium ethyl thiosulfate was hydrolyzed in alkaline solutions of sodium arsenite, and that the reduction of the sulfenic acid by the arsenite then led to the formation of ethyl mercaptan, the product actually isolated. While additional examples of sulfenic acids as postulated intermediates could be enumerated, it will suffice to state that such reports have in common the facts (*a*) that free sulfenic acids were never isolated, and (*b*) that the ability to predict correctly the products obtained in various reactions in which such intermediates have been postulated lends credence to the consideration that these products may stem from a common type of intermediate. The general relationships are indicated below:

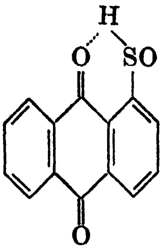


(11)

D. CONCLUSION

In view of the non-isolation of free sulfenic acids, except in the one instance, there seems at present to be inadequate basis for conclusions as to their correct structures. For the purpose of classifying compounds as sulfenyl halides, sulfenamides, etc., the structure RSOH suggests itself as a suitable one. Similarly, it seems justifiable to assume, as an aid to exposition, that structures such as RSOH result as intermediates in certain reactions. However, this does not exclude the possibility that the structure RSOH may be convertible to the "pseudo" form, $\mathrm{R\overset{H}{S}O}$. Since the actual structures of the sulfenic acids are not known with certainty, the mechanisms whereby various sulfenic acid derivatives are converted into products such as the disulfides, sulfinic acids, thiolsulfonic esters, etc., necessarily have only hypothetical status, and will probably warrant deeper consideration than has previously been given to them in the literature. In this regard, the clarification of the analogous problems in the study of selenenic acid derivatives (see page 278) should be of assistance.

The isolation of 1-anthraquinonesulfenic acid by Fries (30) enhances the interest in the inability of Fries and Schürmann to isolate 2-anthraquinonesulfenic acid (32) and 4-substituted 1-anthraquinonesulfenic acids (33). This also indicates that some special structural feature in 1-anthraquinonesulfenic acid renders this compound less subject to conversion into the disulfide, sulfinic acid, and other products. A structure involving hydrogen bonding, such as XI, may be



XI

suggested, but there is no concrete evidence for such an assumption, nor does it explain why 4-amino-1-anthraquinonesulfenic acid is not similarly stabilized, although salt formation with the amino group may be a conflicting factor in this instance. Clearly, more experimental evidence is desirable.

E. NOTATIONS CONCERNING SELENENIC ACIDS AND THEIR DERIVATIVES

The study of sulfenic acids and their derivatives gains added interest in view of the existence of corresponding compounds of selenium.[4] The following notations are intended to point out some of the similarities and contrasts between these two classes of substances.

(*1*) The most extensive recorded studies of selenenic acids and their derivatives are those of Behaghel and coworkers (9, 10, 11, 12, 13). References to earlier investigations are cited in these papers.

(*2*) In contrast to the repeated failures of Zincke and coworkers to isolate substances such as *o*-nitrobenzenesulfenic acid, it was found that *o*-nitrobenzeneselenenic acid and 2,4-dinitrobenzeneselenenic acid could be readily isolated by hydrolysis of the corresponding selenenyl bromides (ArSeBr) or of the acetates ($ArSeOCOCH_3$).

(*3*) Corresponding to the work of Fries (30), 1-anthraquinoneselenenic acid was also prepared (11). The preparation of this acid could not be effected by hydrolysis of 1-anthraquinoneselenenyl bromide, but it was obtained from 1-anthraquinoneselenenyl acetate (compare the isolation of 1-anthraquinonesulfenic acid, page 271).

(*4*) It may be pointed out that the only selenenic acids reported are those which have a nitro group or a quinone oxygen group so situated in the molecule as to suggest a possible stabilization by means of hydrogen bridging, as in the postulated structure (XI) for 1-anthraquinonesulfenic acid. One might be tempted to consider this as indirect evidence for the correctness of such structures. This reasoning, however, has rather obvious pitfalls. For example, it might be expected on this basis that *o*-nitrobenzenesulfenic acid should be isolable, but this is contrary to the known facts (109). Nevertheless, it may be justifiable to follow such a line of thought. It suggests, for example, that it would be interesting to ascertain whether 2-anthraquinoneselenenic acid and *m*- and *p*-nitrobenzeneselenenic acids can be isolated. Apparently, the two latter compounds are not sufficiently stable to permit isolation (11).

(*5*) A very interesting property of the selenenic acids is their definitely amphoteric character. Salt formation was found to take place when these substances were treated either with bases or with a mineral acid. In his studies of sulfenic acids, Zincke (109) implied a similar amphoterism for *o*-nitrobenzenesulfenic acid (see page 328).

(*6*) In addition to the selenenyl halides, and the selenenic acids and their salts, other related compounds, including selenenamides ($RSeNR_2$), acetates ($RSeOCOCH_3$), and cyanides (ArSeCN), have also been adequately characterized and their properties have been investigated. However, in contrast to the ease of preparation of aryl and alkyl sulfenates, reactions which might be expected to lead to the analogous selenenates (RSeOR′) have not been effective in the preparation of these substances. Thus, ethyl *o*-nitrobenzenesulfenate ($o\text{-}NO_2C_6H_4SOC_2H_5$) was easily formed from the sulfenyl halide and sodium ethoxide (see page 325), but the reaction of *o*-nitrobenzeneselenenyl bromide with sodium ethoxide resulted in a mixture of products containing the corresponding diselenide, the selenenic acid, and probably some of the selenophenol (11).

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[4] Tellurium analogs of the sulfenic acid derivatives have also been claimed (69), but the information regarding such compounds seems to be very scant.

(*7*) Definite resemblances between the type reactions of selenenic acid derivatives and those of the sulfenic acids are clearly apparent from a comparative study of examples of each of the two classes of substances. It seems, however, that as a class the selenium derivatives are the more stable group. For example, the selenenyl halides are less readily hydrolyzed than the corresponding sulfenyl halides (12), and another illustration of this tendency toward greater stability is seen in the isolation of a larger number of selenenic acids than of sulfenic acids. As already noted in paragraph 4, however, it may be that the isolation of the selenenic acids, as in the case of 1-anthraquinonesulfenic acid, depends on structural features which are peculiar to those selenenic acids which permit of isolation.

(*8*) The selenenic acids display a characteristic property, associated also with sulfenic acids, in that they tend to undergo disproportionation reactions. In the hydrolysis of benzeneselenenyl bromide, for example, the products obtained are benzeneseleninic acid and phenyl diselenide. It is important to note that the proportions of products actually isolated in this instance corresponded quantitatively to those to be expected if the change occurred as indicated by the equations below (13):

$$C_6H_5SeBr + HOH \rightarrow C_6H_5SeOH + HBr \qquad (12)$$

$$2C_6H_5SeOH \rightarrow C_6H_5Se(O)OH + C_6H_5SeH \qquad (13)$$

$$C_6H_5SeH + HOSeC_6H_5 \rightarrow C_6H_5SeSeC_6H_5 + H_2O \qquad (14)$$

This correlates well with the postulation of the intermediate occurrence of sulfenic acids in similar reactions of sulfenyl halides (see, for example, reference 64).

The above-mentioned contrasts and similarities between selenenic acids and their derivatives, on the one hand, and corresponding sulfenic acid derivatives, on the other, are amplified by additional examples in the papers of Behaghel and coworkers. It is to be seen that the simultaneous development of the studies of these two classes of sulfur and selenium compounds will enhance the interest associated with each group separately, for work in the one suggests possible extensions of experimental studies in the other.

III. THE SULFENYL HALIDES

A. TABULATION OF SULFENYL HALIDES

As has been pointed out by Connor (21), the sulfenyl halides are generally precursors of the other derivatives of sulfenic acids. It therefore seems advisable to consider the methods of preparation and properties of these substances before discussing the other derivatives in detail. Table 1 lists some pertinent informa-

TABLE 1

*Sulfenyl halides**

p-Acetamidobenzenesulfenyl bromide, C_8H_8ONSBr	Not isolated; used in synthesis. From *p*-acetamidophenyl disulfide and bromine in carbon tetrachloride (19).
4-Acetamido-1-naphthalenesulfenyl bromide, $C_{12}H_{10}ONSBr$	Isolated only as the hydrobromide. Pale yellow powder. From 4-acetamido-1-mercaptonaphthalene and bromine in carbon disulfide (116).
4-Acetamido-1-naphthalenesulfenyl chloride, $C_{12}H_{10}ONSCl$	Pale yellow powder. From the mercaptan and chlorine in carbon disulfide or carbon tetrachloride (116).
4-Amino-1-anthraquinonesulfenyl bromide, $C_{14}H_8O_2NSBr$	Isolated only as the hydrobromide. From the disulfide and bromine, or in purer form from the sulfinic acid and hydrogen bromide in glacial acetic acid (33).
1-Anthraquinonesulfenyl bromide, $C_{14}H_7O_2SBr$	Orange needles. M.p. 214°C. From equivalent amounts of 1-anthraquinonyl disulfide and bromine, in chloroform, at boiling point of the reaction mixture. Practically theoretical yield (30). Also from 1-anthraquinonesulfenic acid and hydrogen bromide (30); and by reduction of the sulfinic acid with hydrogen bromide (31).
1-Anthraquinonesulfenyl chloride, $C_{14}H_7O_2SCl$	Orange needles. M.p. 224°C. From the disulfide and chlorine in same manner as the corresponding bromide above (30).
2-Anthraquinonesulfenyl chloride, $C_{14}H_7O_2SCl$	Yellow prisms. M.p. 136°C. From 2-mercaptoanthraquinone or 2-anthraquinonyl disulfide and chlorine, in chloroform, at room temperature (32).
Benzenesulfenyl bromide, C_6H_5SBr	Known only in solution. From thiophenol and bromine (about 20 per cent yield, based on conversion to benzenesulfenodiethylamide). Scission of this sulfenamide with hydrogen bromide gave only phenyl disulfide (64).
Benzenesulfenyl chloride, C_6H_5SCl	Deep red oil. B.p. 58°C./3 mm., 51–54°C./2.5 mm., 73–75°C./9 mm. (corr.). From benzenesulfenodiethylamide and hydrogen chloride in dry ether (42 per cent yield). Also from thiophenol and chlorine in carbon tetrachloride (nearly quantitative yield), and from phenyl disulfide (lower yield) (63, 64).
2-Benzothiazolesulfenyl bromide, $C_7H_4NS_2Br$	Decomposes 80–100°C. From 2-benzothiazolyl disulfide and bromine in carbon tetrachloride (69).

TABLE 1—*Continued*

2-Benzothiazolesulfenyl chloride, $C_7H_4NS_2Cl$	Melts with decomposition at 132–135°C. From 2-benzothiazolyl disulfide or 2-mercaptobenzothiazole and chlorine, in various solvents under anhydrous conditions (26, 69).
2-Benzothiazolesulfenyl iodide, $C_7H_4NS_2I$	Decomposes at 105–125°C. (69).
4,4′-Biphenyldisulfenyl chloride, $C_{12}H_8S_2Cl_2$	Yellow needles or prisms. M.p. 115°C.; decomposes at 140°C. From 4,4′-dimercaptobiphenyl (or the corresponding disulfide or dibenzyl thioether) and chlorine, in carbon tetrachloride or benzene (104, 107).
p-Chlorobenzenesulfenyl chloride, $C_6H_4SCl_2$	B.p. 94°C./6 mm. From thiophenol and chlorine in carbon tetrachloride at 0°C. (37).
1-Chloro-2-naphthalenesulfenyl chloride, $C_{10}H_6SCl_2$	M.p. 74–75°C. From 2-mercaptonaphthalene and chlorine, in chloroform (108; see also reference 64).
4-Chloro-2-nitrobenzenesulfenyl bromide, $C_6H_3O_2NSBrCl$	Yellow-brown needles. M.p. 111°C. From the disulfide and bromine in chloroform (106); also by reduction of 4-chloro-2-nitrobenzenesulfinic acid with hydrogen bromide (31).
4-Chloro-2-nitrobenzenesulfenyl chloride, $C_6H_3O_2NSCl_2$	Golden yellow needles. M.p. 98°C. From the disulfide and chlorine in chloroform in 90 per cent yield (106).
4-Chlorosulfonebenzenesulfenyl chloride, $ClSC_6H_4SO_2Cl$	From the disulfide and chlorine in carbon tetrachloride; product precipitates from reaction mixture. Not isolated, but used in synthesis (101).
2,5-Dibromobenzenesulfenyl bromide, $C_6H_3SBr_3$	Yellow crystals. From the disulfide and bromine. Too unstable to isolate, but used in synthesis (71).
2,5-Dibromobenzenesulfenyl chloride, $C_6H_3SBr_2Cl$	Not isolated, but used in solution for synthetic purposes. From disulfide and chlorine (96).
2,5-Dichlorobenzenesulfenyl chloride, $C_6H_3SCl_3$	Yellow oil. B.p. 92°C./3 mm. From 2,5-dichlorothiophenol and chlorine in carbon tetrachloride at 0°C. (37). Also from the disulfide as golden yellow needles, m.p. 32–33°C. (71).
4,6-Dichloro-1,3-benzenedisulfenyl chloride, $C_6H_2S_2Cl_4$	Yellow needles. M.p. 103°C. From thioresorcinol or from the corresponding dibenzyl thioether, $C_6H_4(SCH_2C_6H_5)_2$, and chlorine in chloroform (104).

TABLE 1—*Continued*

2,5-Dichloro-3-methyl-6-hydroxybenzenesulfenyl chloride, $C_7H_5OSCl_3$	Could not be obtained by various methods (105).
2,4-Dinitrobenzenesulfenyl chloride, $C_6H_3O_4N_2SCl$	M.p. 94–96°C. From the disulfide and chlorine in nitrobenzene (14) or ethylene bromide (59).
4-Hydroxy-1-anthraquinonesulfenyl chloride or bromide, $C_{14}H_6O_3SCl$ (Br)	Could not be prepared from the corresponding disulfide (33).
2-Hydroxy-5-methylbenzenesulfenyl bromide, C_7H_7OSBr	Could not be prepared from the corresponding sulfinic acid and hydrogen bromide. Protection of the phenolic hydroxyl group by forming the carbethoxy ester also did not allow formation of the sulfenyl bromide from the disulfide (104).
Methanesulfenyl iodide, CH_3SI	Postulated as intermediate (see page 300).
4-Methoxy-1-anthraquinonesulfenyl bromide or chloride, $C_{15}H_9O_2SCl$ (Br)	Could not be prepared from the corresponding disulfide (33).
4-Methyl-2-nitrobenzenesulfenyl bromide, $C_7H_6O_2NSBr$	Orange needles. M.p. 95°C. From the disulfide and bromine in carbon tetrachloride. Good yield (114).
4-Methyl-2-nitrobenzenesulfenyl chloride, $C_7H_6O_2NSCl$	Yellow needles. M.p. 90°C. From the disulfide and chlorine in carbon tetrachloride. Yield, about 90 per cent (114, 115).
2-Naphthalenesulfenyl chloride, $C_{10}H_7SCl$	Yellow-red crystalline powder. M.p. 50–60°C. Not obtained pure. From 2-mercaptonaphthalene and one equivalent of bromine. Very unstable (108).
2-Nitrobenzenesulfenyl bromide, $C_6H_4O_2NSBr$	Orange needles. M.p. 85°C. From the disulfide and bromine in carbon tetrachloride (108), or from 2-nitrobenzenesulfinic acid (31).
2-Nitrobenzenesulfenyl chloride, $C_6H_4O_2NSCl$	Yellow needles. M.p. 75°C. From the disulfide and chlorine in carbon tetrachloride at 50–60° C. in 96–97 per cent yield (54, 104).
3-Nitrobenzenesulfenyl chloride, $C_6H_4O_2NSCl$	From the disulfide and chlorine. Properties not described. Used in synthesis (29).
4-Nitrobenzenesulfenyl chloride, $C_6H_4O_2NSCl$	Bright yellow scales. M.p. 52°C. Prepared in same manner as the *o*-isomer above (113).
p-Toluenesulfenyl chloride, C_7H_7SCl	Red oil. B.p. 77.5–78.5°C./2.5 mm. From *p*-thiocresol and chlorine at low temperature in carbon tetrachloride. Light must be avoided, and strictly anhydrous conditions insured. Yield, about 85 per cent. Odor like sulfur dichloride (64).

TABLE 1—*Concluded*

Trichloromethanesulfenyl chloride, Cl_3CSCl	Yellow oil. B.p. 73°C./50 mm., 149°C. at atmospheric pressure. Best prepared from carbon disulfide and chlorine with iodine as halogen carrier. Yield of 65 per cent is attainable. Can be steam distilled with little decomposition. Vapors are lachrymatory and toxic (3, 25, 49).
Trimethylmethanesulfenyl bromide, $(CH_3)_3CSBr$	Known only in solution, but used in synthesis. Prepared from $(CH_3)_3CSN(C_2H_5)_2$ and hydrogen bromide in ether, or from $(CH_3)_3CSHgSC(CH_3)_3$ and 2 moles of bromine. Reddish orange solution in ether. Completely decomposed by attempts to distill (85).
Trimethylmethanesulfenyl chloride, $(CH_3)_3CSCl$	From the diethylamide (see above) and hydrogen chloride at 0°C. Golden yellow solution in ether. Decomposes on distillation at reduced pressure. Could not be prepared from the *tert*-butyl mercaptide (see above) or from *tert*-butyl disulfide and chlorine, because extensive chlorination of the chain occurred in preference to scission of the S—S or S—Hg bonds (85).
Trimethylmethanesulfenyl iodide, $(CH_3)_3CSI$	From the silver or mercury *tert*-butyl mercaptide and iodine in ether solution. Reddish orange ethereal solution. Used in synthesis. Decomposed by distillation at reduced pressures (85).
Triphenylmethanesulfenyl chloride, $(C_6H_5)_3CSCl$	Pale yellow needles or prisms. M.p. 137°C. From triphenylmethyl mercaptan and *one* mole of sulfuryl chloride. Practically quantitative yield recorded (100).

* Yields and physical properties are stated unless these are not available in the references cited.

tion for the sulfenyl halides which were encountered in this literature survey. The list should include practically all of the examples for which indexed or cross-reference record has been made in the literature, but absolute completeness is not claimed. The total number of sulfenyl halides which have been adequately characterized and recorded in the literature is relatively small, but the preparation of this class of substances is surely capable of wide extension. The majority of the known sulfenyl halides are aromatic sulfenyl chlorides and bromides. The few aliphatic examples which are recorded in the literature have been included in table 1. While the preparation of at least two sulfenyl iodides has been reported (69, 87), there appear to be no records of the synthesis of sulfenyl fluorides. An attempt to convert trichloromethanesulfenyl chloride (CCl_3SCl) to the fluoride was not successful (49). The existence of polyfunctional sulfenyl chlorides has been established by the synthesis of 4,4′-biphenyldisulfenyl chloride and

4,6-dichloro-1,3-benzenedisulfenyl chloride (104). Several of the sulfenyl halides reported, such as the trimethylmethanesulfenyl halides, were not isolated, but were obtained in solution and used for synthetic purposes. The evidence for their existence is usually satisfactory.

Zincke, who was the first to prepare substances of this class, designated them as "arylsulfur halides." This name has persisted in many writings, although it seems less satisfactory than the name "sulfenyl halides." In the first place, it implies a parallelism to organometallic compounds, such as organomagnesium halides, which is not quite correct in view of the non-metallic character of sulfur; secondly, it fails to recognize the character of these substances as acid derivatives. Thus, the compound o-$NO_2C_6H_4SCl$ is listed in *Organic Syntheses* as o-nitrophenylsulfur chloride with the subtitle, o-nitrobenzenesulfenyl chloride (54). Other authors would refer to it as 2-nitrophenylchlorothiol (60), 2-nitrobenzenemercaptan chloride, or 2-nitrophenyl chloro sulfide (14). Another variation in nomenclature is the assignment of a special name, such as "thiocarbonyl perchloride" or "perchloromethyl mercaptan" to CCl_3SCl (25, 49), whereas the name "trichloromethanesulfenyl chloride" seems more expressive. The use of the term "sulfenyl halide," which is now preferred by *Chemical Abstracts*, agrees best with the accepted names for the related derivatives of sulfonic and sulfinic acids, and it would seem that its general acceptance should be encouraged.

B. PREPARATION OF SULFENYL HALIDES

In his earlier studies concerning sulfenyl halides, Zincke demonstrated that aromatic sulfenyl chlorides and bromides could be synthesized by means of three essentially similar methods involving the action of chlorine or bromine on aryl disulfides, thiophenols, or aryl benzyl sulfides.

$$ArSSAr + X_2 \rightarrow 2ArSX \tag{15}$$

$$ArSH + X_2 \rightarrow ArSX + HX \tag{16}$$

$$ArSCH_2C_6H_5 + 2X_2 \rightarrow ArSX + C_6H_5CHX_2 + HX \tag{17}$$

In a number of instances, Zincke used these methods alternatively to synthesize the same sulfenyl halide (104).

1. Sulfenyl halides from disulfides

The preparation of sulfenyl halides from aryl disulfides was subsequently extended by Zincke and coworkers (106, 108, 109, 113, 114, 116), and its use by other workers (see table 1) has indicated its rather general application in the synthesis of aromatic sulfenyl chlorides and bromides. The halogenation is conducted at relatively low temperatures, under anhydrous conditions, in solvents such as carbon tetrachloride, chloroform, ethylene chloride, and occasionally benzene, pentane, or other hydrocarbon solvents capable of dissolving both reactants. Although the yields have not always been recorded in the literature, they have been found to be nearly quantitative in some instances and, except where this method encounters serious limitations, are generally indicated as satisfactory. The synthesis of 2-benzothiazolesulfenyl iodide by this method has been claimed in a patent (69), but this is the only record of the synthesis of a sulfenyl iodide by this means. In a paper as early as 1868, Otto (78) anticipated the existence of sulfenyl halides, and reported the preparation of benzenesulfenyl bromide by the reaction of bromine with phenyl disulfide. It was later shown by Zincke, however, that under the conditions employed by Otto (absence of a diluent solvent) nuclear substitution rather than scission of the disulfide linkage occurs, and that the product described by Otto was in reality 4-bromophenyl disulfide and not benzenesulfenyl bromide (104).

The reaction of halogens with disulfides has certain restrictions as a method for the preparation of sulfenyl halides. In the first place, the ease of formation of the sulfenyl halide by reaction of the disulfide with one molar proportion of halogen seems to decrease in passing from chlorine to iodine. It is indicated in the work of Zincke, for example, that in the synthesis of nitrobenzenesulfenyl halides the formation of the sulfenyl chlorides occurred more readily than did that of the sulfenyl bromides; and in the anthraquinone series it has been already indicated (page 274) that in some instances bromine failed to effect the scission of certain symmetrical anthraquinonyl disulfides (33). It therefore seems reasonable to expect that disulfides will not generally be cleaved by the action of one molecular proportion of iodine under the conditions illustrated in table 1 for the similar reactions of chlorine and bromine (85). On the other hand, the action of excess halogen on some disulfides may result in the formation of tetrahalogen derivatives, such as the disulfide tetrabromides and tetraiodides, which on hydrolysis yield thiolsulfonic esters (21, 34). In the presence of hydroxylic solvents or moisture from the air, the action of chlorine may also effect oxidation of the disulfide past the sulfenyl chloride stage and result in the formation of sulfonyl chlorides (33, 88, 97, 98).

Another difficulty in the synthesis of sulfenyl chlorides and bromides from disulfides is the fact that halogenation of the aromatic ring or aliphatic chain may occur in preference to scission of the disulfide linkage (33, 67, 85, 104). This effect is particularly pronounced in the synthesis of aliphatic sulfenyl halides from disulfides, and is largely responsible for the fact that so few of these have been prepared (67). Of the aliphatic sulfenyl halides which have been synthesized, the molecules were so chosen as to minimize the tendency for chain halogenation to occur (table 1). When nitro groups are present in the aromatic nucleus, the tendency for substitution by halogen is greatly reduced, and such sulfenyl halides as *o*-nitrobenzenesulfenyl chloride are particularly easy to prepare in good yields from the disulfides. On the other hand, in the preparation of such compounds as benzenesulfenyl chloride or naphthalenesulfenyl halides, substitution in the aromatic nucleus becomes a problem which requires special attention. The use of low temperatures, dilution of reagents, and exclusion of light and moisture are measures which have been effective in the synthesis of sulfenyl halides in instances where this problem was encountered (63, 67).

There are not sufficient data available to permit generally valid statements to be made in regard to the influence which various groups may have in restricting the effectiveness of the synthesis of sulfenyl halides from disulfides. Obviously, the nitro group does not interfere; the same is probably true of the sulfonyl chloride group, SO_2Cl (101). Groups containing active hydrogen will generally react with the sulfenyl halides formed. Apparently, if the amino group in aminoaryl disulfides is first acetylated, the disulfide linkage may then be cleaved by halogen to yield acetamido aromatic sulfenyl halides (19, 116). Another possible means for protection of the amino group, during cleavage of the disulfide by bromine, may be the formation of the amine hydrobromide (33).

In an excellent paper (67), Lecher and Wittwer have briefly summarized the difficulties attendant on the synthesis of aliphatic sulfenyl halides, as well as such aromatic derivatives as 2-naphthalenesulfenyl halides, in which the nucleus is easily subject to halogenation. Since, in many respects, the sulfenyl thiocyanates (RSSCN) markedly resemble the sulfenyl halides, Lecher and coworkers (66, 67) showed that a number of these could be prepared more readily than the corresponding sulfenyl halides, and suggested the use of the sulfenyl thiocyanates for synthetic work in those instances where the sulfenyl halides proved difficult or impossible to prepare. The sulfenyl thiocyanates will be discussed in some detail in the next section.

2. Sulfenyl halides from thiophenols and mercaptans

The action of chlorine or bromine on thiophenols has been reported as a useful method for the synthesis of aromatic sulfenyl chlorides and bromides (26, 32, 63, 104, 107, 108, 112). Since sulfenyl halides react readily with compounds containing the thiol group, a side reaction is the formation of the disulfides (61, 63, 84, 87, 108, 112, 116). By further reaction of the halogen with disulfide, however, the final product is the sulfenyl halide.

$$RSH + X_2 \rightarrow RSX + HX \tag{18}$$
$$RSH + RSX \rightarrow RSSR + HX \tag{19}$$
$$RSSR + X_2 \rightarrow 2RSX \tag{20}$$

The conditions required in this method, in instances which do not involve secondary difficulties to be described below, are essentially the same as those used in the preparation of sulfenyl halides from disulfides. Thus, in the synthesis of nitro-substituted benzenesulfenyl halides, the use of excess halogen does not cause difficulty, and the yields of such sulfenyl halides obtainable from the nitro-substituted thiophenols are good. In this case, the reactions occur as indicated in equations 18, 19, and 20. In the preparation of a sulfenyl halide such as benzenesulfenyl chloride, however, it is desirable to avoid conversion of the thiophenol to the disulfide. If phenyl disulfide is formed, and the conditions are then made sufficiently vigorous to effect cleavage of the S—S linkage, extensive chlorination of the ring occurs simultaneously (64). In contrast, the conditions required for the formation of the sulfenyl halide by the reaction of the halogen with the thiophenol (equation 18) are mild enough so that ring chlorination is considerably reduced. To avoid disulfide formation, the expedient of gradually adding the thiophenol to a solution of chlorine in an inert solvent maintains a low concentration of the thiophenol; reaction according to equation 19 is thereby reduced to a minimum, and this allows the sulfenyl halide to accumulate in high yield (63). It is to be seen, therefore, that this method for the preparation of sulfenyl halides is subject to essentially the same limitations as is the one employing the disulfides but may be more advantageous, as was illustrated above for the synthesis of benzenesulfenyl chloride. It is interesting to note that if the chlorination of thiophenols is carried out in inert solvents, such as chloroform or carbon tetrachloride, the sulfenyl chlorides are formed; but in glacial acetic acid, sulfonyl chlorides are obtained (107, 110, 115).

As has already been indicated, the preparation of sulfenyl halides from mercaptans encounters difficulties which prevent this method of synthesis from being generally useful. The action of halogens on mercaptides also generally leads to the formation of disulfides, but under controlled conditions it may be used for the preparation of certain sulfenyl halides. Thus, Rheinboldt and coworkers (84, 85, 87) obtained trimethylmethanesulfenyl bromide or the corresponding iodide by reaction of the halogen with *tert*-butyl mercaptides, as shown in equation 21.

$$(CH_3)_3CSHgSC(CH_3)_3 + 2I_2 \rightarrow 2(CH_3)_3CSI + HgI_2 \qquad (21)$$

These workers also indicated that *tert*-amyl mercaptides underwent similar reactions. In a patent citation (92) it was claimed that the reaction of sodium hypochlorite with *tert*-butyl mercaptan allowed the quantitative formation of the corresponding sulfenyl chloride, $(CH_3)_3CSCl$. If this is the case it would be extremely interesting, for one would expect the simultaneous formation of *tert*-butyl disulfide, as well as other products formed by hydrolysis of the sulfenyl chloride.

3. *Sulfenyl halides from sulfides*

The original method employed by Zincke for the synthesis of aromatic sulfenyl chlorides was the reaction between chlorine and an aryl benzyl sulfide, as indicated in equation 17. The conditions required for the scission of the carbon-to-sulfur bond in this type of sulfide are practically identical with those used for the preparation of sulfenyl halides from disulfides. Zincke used this reaction with aryl benzyl sulfides only for the synthesis of aromatic sulfenyl chlorides. Apparently it has not been used by other workers, since it has no particular advantages over the other methods available. It may be noted that while the reaction of chlorine with a methyl aryl sulfide, $ArSCH_3$, leads to the chlorination of the methyl group to give $ArSCCl_3$, the low electronegativity of the benzyl radical permits easy scission of the benzyl sulfides and formation of the sulfenyl halide (104). However, the preparation of 4-methyl-2-nitrobenzenesulfenyl chloride by reaction of chlorine with methyl 4-methyl-2-nitrophenyl sulfide (as well as from the corresponding ethyl sulfide) has been reported (115). Also, not all aryl benzyl sulfides can be converted to aromatic sulfenyl halides by this method. Thus, 2,5-dichloro-3-methyl-6-hydroxybenzenesulfenyl chloride could not be prepared from the corresponding benzyl sulfide (105). It was also observed that if the chlorination of the benzyl sulfides was carried out in glacial acetic acid solution in place of inert solvents, sulfonyl chlorides rather than sulfenyl chlorides were obtained (107, 115).

4. Sulfenyl bromides from sulfinic acids

In 1912, Fries found that the reduction of 1-anthraquinonesulfinic acid with hydrogen bromide, in glacial acetic acid solution, led to the formation of 1-anthraquinonesulfenyl bromide (30). In a later paper (31), this work was extended to show that other aromatic sulfinic acids participated in this reaction. Besides the example already cited, 2-nitrobenzenesulfenyl bromide and 4-chloro-2-nitrobenzenesulfenyl bromide were prepared from the corresponding sulfinic acids. The general equation for the reaction may be written as shown below:

$$\mathrm{RSO_2H + 3HBr \rightarrow RSBr + 2H_2O + Br_2} \qquad (22)$$

In the reaction of hydrogen bromide with other sulfinic acids, under the same conditions as were employed for the reaction with the sulfinic acids mentioned above, reduction to the disulfides rather than to sulfenyl halides was observed. Thus, disulfides were the products obtained by the reaction of hydrogen bromide with the following sulfinic acids: benzenesulfinic acid, *p*-nitrobenzenesulfinic acid, 2-naphthalenesulfinic acid, 5-nitro-1-naphthalenesulfinic acid, and 4-hydroxy-1-anthraquinonesulfinic acid. These reactions may be summarized in equation 23.

$$\mathrm{2RSO_2H + 6HBr \rightarrow RSSR + 4H_2O + 3Br_2} \qquad (23)$$

It was implied (31) that in the latter reactions sulfenyl bromides were formed initially, but that these were unstable and decomposed to yield disulfides. A pertinent observation in this connection was the fact that if 2-nitrobenzenesulfinic acid was reduced by an insufficient amount of the hot hydrogen bromide–acetic acid mixture, 2-nitrophenyl disulfide was obtained, whereas with a larger proportion of the hydrogen bromide solution, the sulfenyl halide was isolated. Since even this relatively stable sulfenyl bromide can be reduced to the disulfide under these conditions, it is not surprising to find that such a conversion occurs at lower temperatures for sulfenyl bromides, whose stabilities have been reported to be of a lower order than that of 2-nitrobenzenesulfenyl bromide. The conversion of the intermediate sulfenyl bromide to the disulfide could occur either by reaction with mercaptans (which may be present in the reaction mixture by decomposition of the sulfinic acids), equation 19, or by thermal decomposition into the disulfide and bromine (equation 24).

$$\mathrm{2RSBr \rightarrow RSSR + Br_2} \qquad (24)$$

Since hydrogen bromide is a rather selective reducing agent, practical advantage of the reaction of this substance with substituted sulfinic acids may be taken to reduce the sulfinic acid group without the simultaneous reduction of other groups, such as the nitro group (31).

In those cases in which sulfenyl bromides were obtained from the sulfinic acids, the reaction took place smoothly and rapidly. The yield of 2-nitrobenzenesulfenyl bromide was stated to be good, but the yields of sulfenyl bromides in the other instances were not reported. Fries (31) also found that "disulfoxides" were easily reduced by hydrogen bromide, in glacial acetic acid solution, either to sulfenyl bromides or to disulfides. Because sulfones are not reduced by hydrogen bromide under these conditions, he considered that the thiolsulfonic ester structure (I, page 271) was not correct, and preferred the symmetrical structure (II, page 271) for substances of the formula $R_2S_2O_2$. In view of later work concerning the structure of the thiolsulfonic esters, this analogy proposed by Fries does not seem valid.

5. Other methods for the preparation of sulfenyl halides

There are a number of other reactions whereby sulfenyl halides are produced. In general, these are not useful as methods of preparation, because the reactants employed are usually best obtained from the sulfenyl halides themselves. However, certain of these reactions may prove useful in particular instances. Thus, sulfenamides may be obtained without resorting to the use of sulfenyl halides (see Section V), and these may then be converted to sulfenyl halides by reaction with hydrogen halides, as shown in equation 25. Some examples of such syntheses are cited in table 1. An interesting one is the preparation of benzenesulfenyl chloride. Earlier attempts to prepare this compound were not satisfactory, and it was variously considered that it was either too unstable to exist or that it could not be prepared from thiophenol or phenyl disulfide without simultaneous chlorination of the ring. Although, as has already been pointed out (page 285), the synthesis from thiophenol or phenyl disulfide can be effected by proper control of the experimental conditions, benzenesulfenyl chloride was first synthesized by scission of benzenesulfenodiethylamide with hydrogen chloride in absolute ether as solvent (63).

$$C_6H_5SN(C_2H_5)_2 + 2HCl \rightarrow C_6H_5SCl + (C_2H_5)_2NH_2Cl \qquad (25)$$

Miscellaneous methods which result in the formation of sulfenyl halides are listed below. Specific instances of these reactions will be considered under later headings.

(*1*) Reaction of hydrogen halide with sulfenic esters:

$$RSOR' + HX \rightarrow RSX + R'OH \qquad (26)$$

(*2*) Reaction of hydrogen halide with sulfenamides, as illustrated in equation 25.

(*3*) Reaction of hydrogen halide with the free sulfenic acids:

$$RSOH + HX \rightarrow RSX + H_2O \qquad (27)$$

The only instances of this type of reaction are to be found in the anthraquinone series and have already been mentioned.

(*4*) Reaction of hydrogen halides or phosphorus pentachloride with sulfenic anhydrides:

$$RSOSR \xrightarrow[\text{(ether)}]{\text{HCl or PCl}_5} RSCl \qquad (28)$$

(*5*) Reduction of certain thiolsulfonic esters with hydrogen bromide under the same conditions as are required for the reduction of sulfinic acids to sulfenyl bromides (31).

C. PHYSICAL PROPERTIES

An interesting characteristic of sulfenyl halides is that those reported are invariably colored. Zincke (108) was the first to observe this general property and ascribed the color to the SX group. Lecher and Holschneider (63) compared the absorption spectrum of sulfur dichloride (ClSCl) with that of benzenesulfenyl chloride and found considerable similarity. They suggested that in sulfur dichloride no further alteration of the molecule can take place, and that the color of this substance as well as of benzenesulfenyl chloride was associated with the chromophoric SCl group. Gebauer-Fülnegg (37) limited his discussion to aromatic derivatives and suggested that in aromatic sulfenyl chlorides, for example, the "loose" nature of the sulfur-to-chlorine bond " . . . seems to cause an alteration of the benzoid structure of the molecule and, as a consequence of the shifting of the valences, a quinoid structure in the benzene ring is approached." He considered that it was this latter structure, and not the sulfenyl chloride group itself, which was responsible for the production of color. While all of the sulfenyl halides are colored, the sulfenamides into which they may be converted may or may not be colored. Zincke had noted that those sulfenamides which contained a nitro group were always colored, and he ascribed their color to the presence of the nitro group. Gebauer-Fülnegg (37) considered that the substitution of the more strongly bonded sulfenamide group, in place of the sulfenyl halide function, largely eliminated the tendency for approach to the "quinoid" structure, and that for this reason the sulfenamides which lacked a nitro group were colorless. If a nitro group was present, however, the tendency for the sulfenamide to approach the quinoid structure was again enhanced and color resulted. A graphic model to depict the approached "quinoid" state was used by this author. According to this reasoning, it would be predicted that the absorption spectra of the nitro-substituted sulfenamides and of the corresponding aromatic sulfenyl halides would be similar. Some of these were compared and found to have definite resemblances,—being nearly identical in the case of 2-nitrobenzenesulfenyl chloride and 2-nitrobenzenesulfenanilide. While these considerations are of interest, and the type of experimental evidence gained in the studies of Gebauer-Fülnegg is valuable, the definite indications that aliphatic sulfenyl halides are also colored (see table 1), and the fact that these were not taken into account by this investigator, considerably lower the validity of his conclusions.

The melting points and distillation temperatures of various sulfenyl halides have been listed in table 1. All of the aromatic sulfenyl halides which contain nitro groups are crystalline solids. Others, such as benzenesulfenyl chloride and its analogs, are liquids which may be distilled at reduced pressure, but which decompose when distilled at ordinary pressures. Although there are only scant indications, it seems that the sulfenyl halides of lower molecular weight are possessed of definite, penetrating odors. For example, benzenesulfenyl chloride is described as having an odor similar to that of sulfur dichloride (63), and Rheinboldt (87) noted that solutions of trimethylmethanesulfenyl iodide and of the corresponding bromide possess sharp irritating odors.

The aromatic sulfenyl halides are generally soluble in solvents such as benzene and chloroform. Water and alcohol are not good solvents for the sulfenyl halides and, in addition, they effect hydrolysis with varying degrees of rapidity. The sulfenyl halides also react with acetone and other compounds containing active hydrogen, so that these are not suitable solvents. There are no specific data given on the solubilities of aliphatic sulfenyl halides. Rheinboldt (85, 87) generally prepared solutions of trimethylmethanesulfenyl halides in absolute ether or carbon tetrachloride, and it may be inferred from the slowness of the reactions of such solutions of the sulfenyl halides with water that their solubilities in the latter are low. This notion is substantiated by the observation that trichloromethanesulfenyl chloride can be steam distilled with little loss by decomposition (25).

D. CHEMICAL PROPERTIES OF SULFENYL HALIDES

The sulfenyl halides enter into a variety of reactions which have already established their value as synthetic intermediates. In the following discussion, these reactions will be classified under the following headings: (*1*) oxidations, (*2*) formation of disulfides, (*3*) thioalkylation and thioarylation reactions, (*4*) hydrolytic reactions, (*5*) exchange reactions with metallic salts, and (*6*) formation of sulfenamides. A section concerning sulfenyl halides as postulated intermediates has also been included.

In his fundamental studies, Zincke found that the general reactions of aromati sulfenyl chlorides and bromides were essentially similar. In nearly all the synthetic studies, however, the sulfenyl chlorides rather than the bromides hav been used. Besides the work of Zincke there have been no extensive, systemati studies of the comparative reactivities of sulfenyl halides toward specific reagents Nevertheless, significant differences have been noted in some instances. Fo example, Fries and Schürmann (32) found that 2-anthraquinonesulfenyl chloride as well as the corresponding bromide, showed remarkably greater reactivitie than the isomeric 1-anthraquinonesulfenyl halides in reactions with acetone glacial acetic acid, and acetoacetic ester, but such differences were not noted i reactions with ammonia, amines, and phenols. Similarly, *p*-nitrobenzenesulfeny chloride was found to be decidedly more subject to hydrolytic decompositio than was the ortho isomer (113), and 1-chloro-2-naphthalenesulfenyl chlorid was far more stable than 2-naphthalenesulfenyl chloride itself (108). It ha also been clearly established that the halogen atom in sulfenyl halides is generall decidedly reactive, and seems, at least in some instances, to be even more rea tive than is the halogen atom in corresponding sulfonyl halides. The majorit of reactions involving sulfenyl halides occur rapidly; in many instances the occur spontaneously at room temperature.

Zincke (109, 113) emphasized the observation that in some reactions aromat sulfenyl halides displayed properties of acid halides, whereas, in others, their behavior recalled that of diazonium salts (compare, for example, equations 3 and 4, page 272). Gebauer-Fülnegg (37) also commented on the dual behavior of the chlorine atom in aromatic sulfenyl chlorides. He suggested that these substances behaved as "electromers," the chlorine atom sometimes acting as a negative group, while in other reactions it displayed properties characteristic of positive chlorine, as in hypochlorites or chloroamines.[5] Thus, in inert solvents, even with rigorous exclusion of moisture, Gebauer-Fülnegg recorded that reaction with silver nitrate precipitated silver chloride, while in reactions with iodides, free iodine was liberated. Rather than to ascribe such differences to the existence of two electromeric species of the sulfenyl chloride, it would seem preferable to consider that, depending on the nature of the reagents and the experimental conditions, the mechanism of the reaction differs,—occurring by an ionic mechanism in some cases, and by a free-atom mechanism in others (see also page 298).

Although both sulfenyl chlorides and bromides are highly reactive, it appears that the former are decidedly more stable with respect to thermal decomposition (19, 64, 71, 84, 85). Sulfenyl iodides, however, are virtually unknown, and very little can therefore be said about their properties. Apparently, the tendency for these to undergo thermal decomposition is very great. The few facts which are known about trimethylmethanesulfenyl iodide in solution (84, 87) will be mentioned below (see also table 1), but the thermal instability of this substance has thus far precluded its isolation.

1. *Oxidation reactions*

Relatively little work has been done on the oxidation of sulfenyl halides. Zincke and Farr (109) found that *o*-nitrobenzenesulfenyl chloride reacted with warm nitric acid (d = 1.4), in glacial acetic acid solution, to yield a readily separable mixture of the corresponding sulfonyl chloride and sulfonic acid. *p*-Nitrobenzenesulfenyl chloride reacted similarly, but in this case it was observed that some of the "disulfoxide" was also formed (113). 1-Chloro-2-naphthalenesulfenyl chloride (108) and 4,4′-biphenyldisulfenyl chloride (107) were oxidized to the corresponding sulfonyl chlorides, either by hot nitric acid, or by chlorine in glacial acetic acid solution. The fact that chlorine, in acetic acid, converts these sulfenyl chlorides, as well as 4-methyl-2-nitrobenzenesulfenyl chloride (114), to the sulfonyl chlorides recalls the observations that disulfides, thiophenols, and aryl benzyl sulfides also react with chlorine in glacial acetic acid solution to give sulfonyl chlorides. This indicates the possibility that the sulfenyl chlorides may be intermediates in these reactions—since, as has already possessed of definite, penetrating odors. For example, benzenesulfenyl chloride is described as having an odor similar to that of sulfur dichloride (63), and Rheinboldt (87) noted that solutions of trimethylmethanesulfenyl iodide and of the corresponding bromide possess sharp irritating odors.

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[5] Since the chloroamines (ArNHCl) are not appreciably colored, Gebauer-Fülnegg used the above analogy between sulfenyl chlorides and chloroamines in support of his conclusion that the SCl group, as such, is not chromophoric. This is questionable, for it assumes that color depends on the nature of the chlorine atom rather than on the group as a whole. In this connection, it may be pointed out that the thiocarbonyl group is itself a chromophore (thiobenzophenone and thioacetophenone, for example, are blue), and it may be that the attachment of the chlorine atom results in a new chromophoric group.

The aromatic sulfenyl halides are generally soluble in solvents such as benzene and chloroform. Water and alcohol are not good solvents for the sulfenyl halides and, in addition, they effect hydrolysis with varying degrees of rapidity. The sulfenyl halides also react with acetone and other compounds containing active hydrogen, so that these are not suitable solvents. There are no specific data given on the solubilities of aliphatic sulfenyl halides. Rheinboldt (85, 87) generally prepared solutions of trimethylmethanesulfenyl halides in absolute ether or carbon tetrachloride, and it may be inferred from the slowness of the reactions of such solutions of the sulfenyl halides with water that their solubilities in the latter are low. This notion is substantiated by the observation that trichloromethanesulfenyl chloride can be steam distilled with little loss by decomposition (25).

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[5] Since the chloroamines (ArNHCl) are not appreciably colored, Gebauer-Fülnegg used the above analogy between sulfenyl chlorides and chloroamines in support of his conclusion that the SCl group, as such, is not chromophoric. This is questionable, for it assumes that color depends on the nature of the chlorine atom rather than on the group as a whole. In this connection, it may be pointed out that the thiocarbonyl group is itself a chromophore (thiobenzophenone and thioacetophenone, for example, are blue), and it may be that the attachment of the chlorine atom results in a new chromophoric group.

2. Formation of disulfides

In a number of reactions of sulfenyl halides, disulfides are obtained as the main products. The mercaptans or mercaptides may be intermediate products in such reactions, but the ease with which each of these reacts with sulfenyl halides to give disulfides probably explains why the latter are the products actually isolated. A few examples of such reactions follow. *o*-Nitrobenzenesulfenyl chloride, dissolved in dry ether, reacted with thiophenol to give a nearly quantitative yield of the corresponding disulfide (61). Benzenesulfenyl chloride reacted with zinc to give phenyl disulfide (63). 2-Thionaphthol or its mercury derivative, $Hg(SC_{10}H_7)_2$, readily reacted with ethereal solutions of trimethylmethanesulfenyl iodide to give the unsymmetrical disulfide (87). Trimethylmethanesulfenyl iodide reacted with magnesium or mercury to form *tert*-butyl disulfide in nearly quantitative yield. The formation of this disulfide from the sulfenyl iodide also occurred upon shaking with water or upon heating. Even at low temperatures, slow decomposition occurred; iodine was eliminated, and *tert*-butyl disulfide was formed. At room temperatures, or at the boiling point of ethereal solutions, this change occurred much more rapidly. However, anhydrous ether solutions of the sulfenyl iodide could be kept at 0°C. for several days. With aqueous sodium thiosulfate solutions, reduction to *tert*-butyl disulfide was also the main reaction. In this case it was observed that the reduction was accelerated by exposure to sunlight (87). In absolute alcohol solution, at room temperatures, potassium hydrogen sulfide reduced 2-nitrobenzenesulfenyl chloride to the corresponding disulfide (24). The formation of disulfides by the reduction of sulfinic acids with hydrogen bromide or hydrogen iodide, or by the reduction of 1-anthraquinonesulfenic acid with hydrogen iodide (31), possibly involves the sulfenyl halides as intermediates. Disulfides were also reported as products in the reactions of aromatic sulfenyl halides with certain compounds which contain active methylene groups, such as benzyl cyanide, malonic ester, and acetonylacetone (106), but the exact nature of these reactions has not been carefully established (see also page 294). Iodide ion can also effect the reduction of sulfenyl halides to disulfides. Thus, benzenesulfenyl chloride, dissolved in carbon tetrachloride, reacted quantitatively with an aqueous solution of potassium iodide to liberate one equivalent of iodine and to form phenyl disulfide (16). In hydrolytic reactions of sulfenyl halides, disulfides have often been observed among the products, but such reactions will be enumerated in a later paragraph (page 296). Heating of sulfenyl halides generally leads to disulfides; the process seems to be facilitated in the presence of a tertiary amine. Thus, 4-acetamino-1-naphthalenesulfenyl bromide hydrobromide decomposed to the disulfide when heated (116), and 2-nitrobenzenesulfenyl bromide when heated with pyridine likewise gave 2-nitrophenyl disulfide (74). Sulfenyl halides also react with hydrogen sulfide to form trisulfides. Thus, the reaction of benzenesulfenyl chloride with hydrogen sulfide results in the formation of phenyl trisulfide, $C_6H_5SSSC_6H_5$. Benzenesulfenyl thiocyanate (C_6H_5SSCN) gives the same trisulfide by reaction with hydrogen sulfide (62).

3. Thioalkylation and thioarylation reactions

Under this heading will be included those reactions of the sulfenyl halides which lead to the formation of a sulfur-to-carbon bond. The nature of the groups which may be attached to the sulfur atom by these reactions may be aliphatic or aromatic, and they may be variously substituted. Furthermore, it is probable that the formation of the sulfur-to-carbon bond sometimes results from a secondary process, such as the rearrangement of a sulfenamide to an amino sulfide, rather than from direct replacement of the halogen atom from the sulfenyl halide by the organic radical.

(a) Reactions with Grignard reagents

Lecher and coworkers (64) found that benzenesulfenyl chloride and *p*-toluenesulfenyl chloride reacted smoothly with ethereal solutions of phenylmagnesium bromide to give 65–70 per cent yields of the corresponding sulfides.

$$C_6H_5MgBr + ArSCl \rightarrow C_6H_5SAr + MgBrCl \qquad (29)$$

The reaction was suggested as a suitable method for the preparation of unsymmetrical organic sulfides.

(b) Additions to olefins

The formation of "mustard gas," $ClCH_2CH_2SCH_2CH_2Cl$, from ethylene may involve 2-chloroethanesulfenyl chloride as an intermediate in the manner indi cated below:

$$CH_2{=}CH_2 + SCl_2 \rightarrow ClCH_2CH_2SCl \xrightarrow{CH_2=CH_2} ClCH_2CH_2SCH_2CH_2Cl \qquad (30)$$

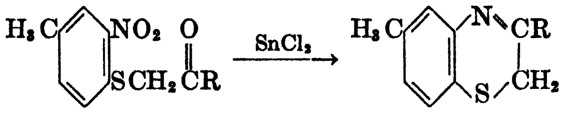
This would suggest that other sulfenyl halides could add to the ethylenic bond Lecher and coworkers (64) found that benzenesulfenyl chloride and *p*-toluenesulfenyl chloride reacted with ethylene, in carbon tetrachloride solution, to give the corresponding 2-chloroethyl sulfides.

$$CH_2{=}CH_2 + p\text{-}CH_3C_6H_4SCl \rightarrow ClCH_2CH_2SC_6H_4CH_3 \qquad (31)$$

These reactions occurred at room temperatures and the yields of products were high. 2-Nitrobenzenesulfenyl chloride underwent a similar addition to ethylene at an elevated temperature (100°C.). 2-Nitrobenzenesulfenyl chloride and 2,4-dinitrobenzenesulfenyl chloride undergo similar addition reactions with cyclohexene (59).

(c) Reactions with ketones and compounds containing active methylene groups

Zincke (104, 106, 109, 113, 114, 116) demonstrated that the aromatic sulfenyl chlorides reacted readily with ketones such as acetone and acetophenone, as well as with diethyl ketone and acetoacetic ester. The products were readily isolated and may be generally formulated as ketones in which hydrogen from an active methylene or methyl group has been replaced by an ArS— radical. These reactions occurred when the reactants were gently heated, either alone, or in solution with an inert solvent such as chloroform. For example, when 2-nitro-4-methylbenzenesulfenyl chloride reacted with acetone and acetophenone (114), compounds such as XII (R = methyl or phenyl) were obtained. Upon reduction of the nitro group of XII with stannous chloride ring closure occurred, and this afforded a method for the synthesis of 3-substituted 1,4-benzothiazines such as XIII (106, 114). Additional examples of the reactions of sulfenyl chlorides with methyl ketones have been found, and will be reported in the near future (59).



XII XIII (32)

The sulfenyl bromides do not necessarily react with ketones in a similar manner. For example, 2-nitro-4-methylbenzenesulfenyl bromide reacted with acetone, causing bromination of the latter and yielding 2-nitro-4-methylphenyl disulfide. The formation of a compound corresponding to XII was, however, not observed (114). The greater ease of thermal decomposition of the sulfenyl bromide, in comparison with the corresponding sulfenyl chloride, may account for this observed difference. Zincke has furnished numerous other examples of the reactions of various aromatic sulfenyl chlorides with ketones to form compounds such as XII. Introduction of the ArS— group also occurred readily upon reaction of the sulfenyl chlorides with the sodium or copper derivative of acetoacetic ester (32, 106). While reaction with acetoacetic ester itself may occur as expected (106), it is not always smooth (32).

In the same way, while 2-nitro-4-chlorobenzenesulfenyl chloride reacted with a number of methyl ketones, as well as with diethyl ketone and acetylacetone, as would be expected from the above examples, its reactions with acetonylacetone, benzyl cyanide, and malonic ester did not lead to the expected sulfides, but rather to the corresponding disulfide $(NO_2ClC_6H_3S)_2$ and various more complex products from the carbonyl components. Acetaldehyde also reacted with the above sulfenyl chloride to yield the disulfide, paraldehyde, and other products (106).

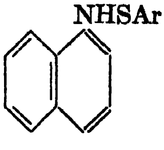
(d) Reactions with dimethylaniline, naphthylamines, phenols, and benzene

With activated aromatic nuclei, such as in naphthols, phenols, dimethylaniline, and naphthylamines, reactions with aromatic sulfenyl halides have been reported to introduce an ArS— group into the aromatic nucleus. The following examples may demonstrate the scope and nature of these reactions.

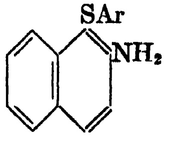
(*1*) As already indicated (page 272), 1-anthraquinonesulfenyl bromide reacted with β-naphthol at 110°C. to eliminate hydrogen bromide and to form 1-anthraquinonyl 2-hydroxy-1-naphthyl sulfide (equation 4). Anthraquinonesulfenyl halides also reacted especially easily with resorcinol to introduce the anthraquinonylthio radical in position 4 of the resorcinol molecule.

(*2*) Heating 1-anthraquinonesulfenyl bromide with an equal weight of dimethylaniline on the steam bath for 3 hr. yielded 1-anthraquinonyl 4-dimethylaminophenyl sulfide (32). 2-Nitrobenzenesulfenyl chloride reacted similarly when refluxed for a short time with dimethylaniline (109).

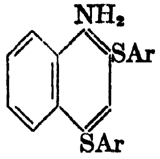
(*3*) With α- and β-naphthylamines, there may be obtained sulfenamides such as XIV. However, if the reaction between the sulfenyl halide and amine was effected in hot glacial acetic acid, amino sulfides such as XV and XVI were formed instead (109, 114).



XIV

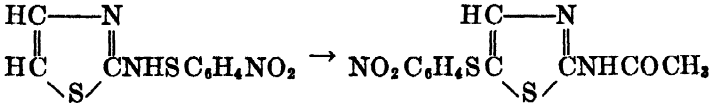


XV



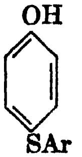
XVI

It is likely that the formation of the amino sulfides involves rearrangements of the sulfenamides (see page 321). Bambas (5) found that the reaction of *p*-nitrobenzenesulfenyl chloride with 2-thiazolylamine in glacial acetic acid at 20°C., followed by heating with acetic anhydride at 85°C., gave 4-nitrophenyl 2-acetamino-5-thiazolyl sulfide (XVIII). It was suggested that the formation of the sulfide involved rearrangement, accompanied by acetylation, of XVII to XVIII.

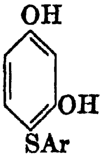


XVII XVIII (33)

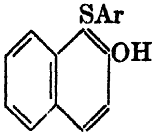
Phenol, resorcinol, *o*- and *m*-cresols, catechol, thymol, and the naphthols reacted readily with aromatic sulfenyl chlorides to give hydroxy sulfides (28, 29, 64, 106, 109, 113, 114). The reactions are similar to those which occur with dimethylaniline, and the products obtained may be exemplified by structures XIX to XXII.



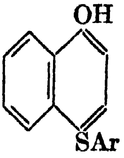
XIX



XX



XXI



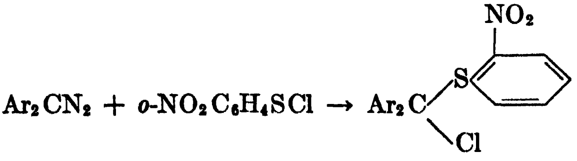
XXII

The substitution of the ArS— group always occurred in a position para to the phenolic hydroxyl group. While reactions with phenols which possess free para-positions, such as those mentioned above, occurred readily, it was found (114) that 2-nitro-4-methylbenzenesulfenyl chloride did not react with *p*-cresol or hydroquinone, nor did the substitution of the ArS— group occur with simple phenyl ethers such as anisole. At least superficially, the above reactions of sulfenyl halides appear similar to the coupling reactions of phenols with diazonium salts. Various other examples of sulfide formation by the reaction of sulfenyl halides with phenols are included in the papers of Zincke and also of Foss and coworkers (28, 29). Such reactions serve as suitable preparative methods for the hydroxy sulfides. It may be pointed out, however, that with the exception of the work of Fries (30) and of Stevenson and Smiles (96), nearly all of the reactions of sulfenyl halides with phenols have been carried out with nitro-substituted benzenesulfenyl chlorides. This is probably a result of the greater ease of preparation of these chlorides, and also of their lesser tendency to undergo hydrolytic decomposition.

It has also been reported that the introduction of the ArS— radical into the benzene nucleus may be effected by reaction of the hydrocarbon with 1-anthraquinonesulfenyl chloride in the presence of aluminum chloride (32). However, Lecher and coworkers (64) reported that attempts to use benzenesulfenyl chloride and *p*-toluenesulfenyl chloride in modified Friedel–Crafts syntheses were not successful. An additional interesting example is the reported reaction between trichloromethanesulfenyl chloride and benzene, in the presence of aluminum chloride, to yield thiobenzophenone (100).

(e) Reactions with diazomethanes

Schönberg and coworkers (90, 91) found that aromatic sulfenyl chlorides reacted smoothly with diazomethane and diaryl diazomethanes to form hemimercaptol halides, as indicated in equation 34.



(34)

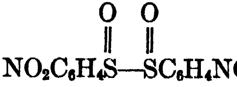
These reactions occurred spontaneously when the sulfenyl chloride was added to an ethereal solution of the diazomethane. The yields of products reported for several instances were satisfactory.

4. Hydrolytic reactions

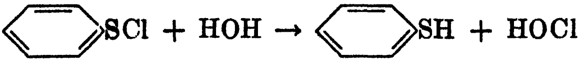
Under this heading will be included the reactions of sulfenyl halides with hydroxylic solvents such as water, alcohols, or glacial acetic acid, under neutral, acidic, or basic conditions. In a few instances, the products reported were those which would be expected from a metathetic exchange of groups (see, for example, the reaction of 1-anthraquinonesulfenyl bromide with methanol, page 271). However, the great majority of the examples cited in the literature list products which cannot be accounted for by such a simple expression. In most of the recorded examples, there were reported disulfides, sulfinic acids, the so-called "disulfoxides" or thiolsulfonic esters, sulfenic anhydrides, and in some cases sulfonyl halides and sulfonic acids. Some typical illustrations follow: Zincke and Farr (109) reported that 2-nitrobenzenesulfenyl chloride reacted with cold water to give the sulfenic anhydride. This hydrolysis was found to be reversible, for by the action of concentrated hydrochloric acid on the sulfenic anhydride, the sulfenyl chloride was once more obtained.

$$2NO_2C_6H_4SCl + H_2O \leftrightarrows (NO_2C_6H_4S)_2O + 2HCl \tag{35}$$

When 2-nitrobenzenesulfenyl chloride was dissolved in cold methyl or ethyl alcohol, it decomposed slowly to give the disulfide, $(NO_2C_6H_4S)_2$, the disulfoxide, formulated as $NO_2C_6H_4\overset{\overset{O}{\|}}{S}—\overset{\overset{O}{\|}}{S}C_6H_4NO_2$, and a smaller amount of 2-nitrobenzenesulfinic acid. If the sulfenyl chloride was boiled with methyl alcohol, however, the disulfide and the sulfinic acid were the main products. With aqueous methyl alcohol, at reflux temperature, considerable amounts of the disulfide and orthanilic acid were obtained, as well as some of the sulfinic acid and *o*-nitrobenzenesulfonic acid. With dilute sodium hydroxide solution, the main product of the reaction was 2-nitrobenzenesulfinic acid and there was also formed a smaller quantity of 2-nitrophenyl disulfide. Lecher and Holscheider (64) found that reaction of benzenesulfenyl chloride with cold dilute aqueous sodium hydroxide solution gave nearly the theoretically expected quantities of phenyl disulfide and benzenesulfinic acid. Miller and Smiles (71) recorded a similar reaction for 2,5-dichlorobenzenesulfenyl chloride. The hydrolytic reactions of the anthraquinonesulfenyl halides, in which products similar to those listed above were reported, have already been mentioned (see Section I and references 30, 31, 32, 33). Other nitrobenzenesulfenyl halides undergo reactions similar to those described for *o*-nitrobenzenesulfenyl chloride. For example, *p*-nitrobenzenesulfenyl chloride (113) was readily decomposed into a mixture of the disulfide and "disulfoxide" when exposed to moist air. The reaction of this sulfenyl halide with methyl or ethyl alcohol yielded, first, the sulfenic anhydride, $(NO_2C_6H_4S)_2O$, but on longer contact with the alcohols there was formed a mixture of the disulfide and "disulfoxide". With dilute sodium hydroxide solution, the main product was *p*-nitrobenzenesulfinic acid. Under the same circumstances, 2-nitro-4-methylbenzenesulfenyl chloride (114) and 2-nitro-4-chlorobenzenesulfenyl chloride (106) reacted in the same manner as the examples already cited.



It is possible to correlate the various products observed in the above reactions by assuming that free sulfenic acids are formed as intermediates, and that these can then undergo disproportionation into products which may interact among themselves as shown in equations 11 (page 276). While there are several indications which substantiate the belief that sulfenic acids or their salts occur as intermediate products in the hydrolysis of sulfenyl halides, the representation in equations 11 is simply a geometrical model which predicts the main products observed, but gives no information as to the mechanisms whereby the various reactions occur. On the basis of their studies of the hydrolysis of sulfur dichloride, Böhme and Schneider (16) proposed that the first step in the hydrolysis of sulfenyl chlorides is the formation of the thiophenol and hypochlorous acid.



(36)

They considered that the hypochlorous acid then acts in its capacity as an oxidizing agent to form products which interact among themselves to give the ones actually isolated. One of their main arguments in support of this viewpoint was the observation that 2 moles of benzenesulfenyl chloride reacted quantitatively with aqueous potassium iodide solution to yield 1 mole of iodine. On this basis, they proposed that the charge on the chlorine atom is positive and that the formula for the sulfenyl halide should be written $C_6H_5\overset{-}{S}\overset{+}{Cl}$. While this type of evidence may be in the right direction, a more complete, experimentally verified statement of the mechanism of these reactions is still to be advanced. One additional reaction of interest is the conversion of trichloromethanesulfenyl chloride to thiophosgene (3, 49). Böhme and Schneider (16) interpreted the hydrolysis to occur as indicated in equation 37.

$$Cl_3CSCl \xrightarrow{H_2O} HOCl + Cl_3CSH \rightarrow HCl + Cl_2C{=}S \qquad (37)$$

In practice the reaction is carried out in the presence of tin and hydrochloric acid and is looked upon by other authors (25) as a reduction by hydrogen (see also reference 83).

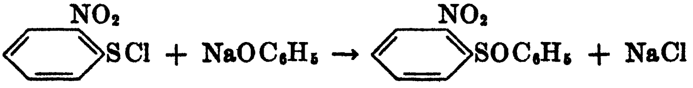
$$Cl_3CSCl + 2H \rightarrow Cl_2C{=}S + HCl \qquad (38)$$

Certain other hydrolytic reactions which lead to sulfenic anhydrides, sulfenates, and sulfenamides will be considered when the methods of preparation of these sudstances are taken up.

5. Exchange reactions with metallic salts

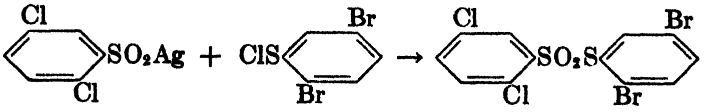
The sulfenyl halides undergo a variety of reactions with metallic salts. Although it is true that, in some instances, only a few examples of a certain reaction may be known, the majority of these should prove to be of general character.

(*a*) With sodium alkoxides or phenoxides, the formation of the alkyl and aryl sulfenates is reported. A typical reaction from the work of Zincke (109) is shown below (see also Section VI).



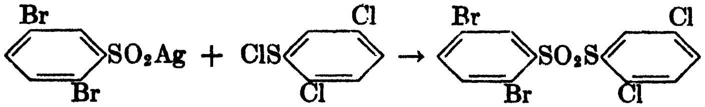
(39)

(*b*) Silver salts of sulfinic acids react to give thiosulfonic esters. Thus, benzenesulfenyl chloride reacted with silver benzenesulfinate, in dry ether, to give a nearly quantitative yield of the product designated as "diphenyl disulfoxide" (64). Zincke (109) described a similar reaction for 2-nitrobenzenesulfenyl chloride and silver benzenesulfinate. A particularly interesting example of this reaction was furnished by Miller and Smiles (71). These workers found that compounds XXIII and XXIV were isomeric but were distinctly different. The formation of these two compounds, as shown in equations 40 and 41, was proposed as evidence for the correctness of the unsymmetrical structure for thiolsulfonic esters (see also footnote 3, page 271).



(40)

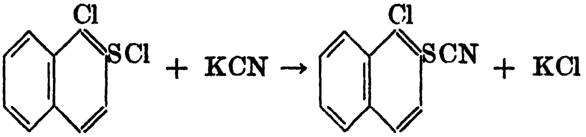
XXIII



(41)

XXIV

(*c*) With potassium cyanide in glacial acetic acid, the sulfenyl halides react readily to give thiocyanates (106, 108, 109, 113).



(42)

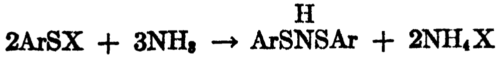
(*d*) With metal thiocyanates, there are formed the sulfenyl thiocyanates (see Section IV).

(*e*) The formation of disulfides by reaction of sulfenyl halides with mercaptides has already been mentioned (page 286).

$$\mathrm{RSX} + \mathrm{R'SM} \rightarrow \mathrm{RSSR'} + \mathrm{MX} \qquad (43)$$

6. *Formation of sulfenamides*

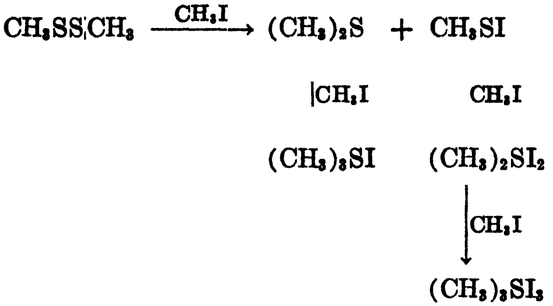
The sulfenyl halides react with ammonia and amines to yield sulfenamides. These reactions will be dealt with in detail under the preparation of sulfenamides (page 314). With excess of the sulfenyl halides, sulfenimides may be obtained (see table 3 and page 319).



$$2\mathrm{ArSX} + 3\mathrm{NH_3} \rightarrow \mathrm{ArS}\overset{\mathrm{H}}{\mathrm{N}}\mathrm{SAr} + 2\mathrm{NH_4X} \qquad (44)$$

7. *Sulfenyl halides as postulated intermediates*

Sulfenyl halides have been postulated as intermediate products in certain reactions. Their probable rôle as intermediates during the reduction of sulfinic acids and thiolsulfonic esters to disulfides by means of hydrogen bromide has been mentioned previously. The reduction of thiolsulfonic esters with hydrogen iodide gives only disulfides. Although sulfenyl iodides may occur as intermediates, these have never been isolated (71). Another instance is the postulation of methanesulfenyl iodide (95) to explain the very easy formation of equivalent amounts of trimethylsulfonium iodide and trimethylsulfonium triiodide in the reaction of methyl iodide with methyl disulfide, as shown below:



$$\begin{tikzcd} CH_3SSCH_3 \arrow[r, "CH_3I"] & (CH_3)_2S \arrow[d, "CH_3I"] & + \; CH_3SI \arrow[d, "CH_3I"] \\ & (CH_3)_3SI & (CH_3)_2SI_2 \arrow[d, "CH_3I"] \\ & & (CH_3)_3SI_3 \end{tikzcd} \qquad (45)$$

The possible rôle of 2-chloroethanesulfenyl chloride in the synthesis of "mustard gas" has already been mentioned (page 293). It is probable, also, that trichloromethanesulfenyl chloride (CCl_3SCl) is an intermediate product in the preparation of carbon tetrachloride from carbon disulfide and chlorine (49). Sulfenyl chlorides have also been postulated in the synthesis of diphenylene disulfides (thianthrenes) by reaction of benzenoid compounds and sulfur monochloride (30) (*cf.* also the formation of thioxanthones and thianthrenes from disulfides, page 275).

IV. THE SULFENYL THIOCYANATES

The original studies of the sulfenyl thiocyanates (RSSCN) are recorded in two papers by Lecher and coworkers (66, 67). The striking similarities between thiocyanate and halide ions, as well as between thiocyanogen, $(SCN)_2$, and the elementary halogens (X_2), led these workers to consider that the sulfenyl thiocyanates should be similar in their properties to the sulfenyl halides. Furthermore, in view of the difficulties encountered in the synthesis of certain sulfenyl halides (see Section III,B), it was suggested that the corresponding sulfenyl thiocyanates might prove easier to prepare. As the following discussion will show, these expectations were realized in some measure.

A. PREPARATION OF SULFENYL THIOCYANATES

The sulfenyl thiocyanates may be prepared in two ways: (*a*) By reaction of a sulfenyl halide with a metal thiocyanate:

$$RSCl + KSCN \rightarrow RSSCN + KCl \qquad (46)$$

(*b*) By reaction of a thiophenol or mercaptan with thiocyanogen:

$$RSH + (SCN)_2 \rightarrow RSSCN + HSCN \qquad (47)$$

Method (*a*) illustrates a general property of the sulfenyl halides and affords a method for the preparation of sulfenyl thiocyanates in those cases where the halide is available, but is, obviously, of no assistance in those instances where the sulfenyl thiocyanates are required to serve as substitutes for sulfenyl halides which cannot be easily prepared. In the examples studied (66), the reaction of a sulfenyl halide with the thiocyanate was readily achieved by shaking equivalent amounts of the reactants for extended periods in a solvent such as benzene. The yields of 2-nitrobenzenesulfenyl thiocyanate and of triphenylmethanesulfenyl thiocyanate, from the corresponding sulfenyl chlorides, were found to be practically quantitative. 2,4-Dinitrobenzenesulfenyl thiocyanate has been similarly prepared (59).

The preparation of sulfenyl thiocyanates from the mercaptan or thiophenol by reaction with thiocyanogen also seems to be capable of general application. This reaction probably proceeds by the same mechanism as does the reaction between a mercaptan and halogen, but seems to have two points in its favor. In the first place, the reaction between the sulfenyl thiocyanate and the unreacted mercaptan, to give the disulfide (equation 48), takes place sufficiently slowly so that with an excess of thiocyanogen present the formation of the sulfenyl thiocyanate is the main reaction.

$$\mathrm{RSSCN} + \mathrm{HSR'} \rightarrow \mathrm{RSSR'} + \mathrm{HSCN} \qquad (48)$$

Secondly, the tendency for nuclear or chain substitution of hydrogen by thiocyanogen is lower than is the corresponding tendency for halogenation to occur. Thus, the major difficulties associated with the synthesis of sulfenyl halides from mercaptans are largely discounted in the synthesis of sulfenyl thiocyanates. In contrast to the failures of attempts to prepare sulfenyl halides, such as ethanesulfenyl chloride, it was therefore found possible to synthesize the corresponding sulfenyl thiocyanate.

In the preparation of sulfenyl thiocyanates by method (*b*), a slightly greater than 1 molar proportion of thiocyanogen (prepared in absolute ether solution by reaction of lead thiocyanate with bromine) is reacted with the chosen mercaptan or thiophenol at low temperatures. The reaction is complete in a short time. The excess thiocyanogen and thiocyanic acid are separated by decomposing the reaction mixture with ice, and the sulfenyl thiocyanate is then isolated from the ether solution (67).

B. TABULATION OF SULFENYL THIOCYANATES

A number of examples of sulfenyl thiocyanates are listed in table 2.

C. PROPERTIES OF SULFENYL THIOCYANATES

Some of the physical characteristics of the sulfenyl thiocyanates have been recorded in table 2. In contrast to the sulfenyl halides, the sulfenyl thiocyanates are not necessarily colored. Thus, while 2-nitrobenzenesulfenyl thiocyanate and 2-naphthalenesulfenyl thiocyanate are yellow, ethanesulfenyl thiocyanate and benzenesulfenyl thiocyanate are colorless. While the 2-nitrobenzene and the 2-naphthalene derivatives were found to be odorless, the sulfenyl thiocyanates derived from ethane and benzene possessed sufficiently remarkable odors to warrant special notice.

The thermal stability of ethanesulfenyl thiocyanate was found to be sufficiently great to permit purification by distillation at reduced pressure (see table 2). On standing at room temperature, most of the sulfenyl thiocyanates tend to decompose. Ethanesulfenyl thiocyanate was the most difficult to keep, and underwent extensive decomposition in a period of half an hour. Benzenesulfenyl thiocyanate was also very subject to decomposition on keeping. 2-Naphthalenesulfenyl thiocyanate, however, was fairly stable and underwent only slight decomposition in a period of weeks. In ether solution, the above compounds could be kept for longer periods. 2-Nitrobenzenesulfenyl thiocyanate, however, is a very stable compound, which requires no special storage precautions and may be recovered unchanged after heating in ethylene bromide solution at 90°C. for 2 hr. (59).

TABLE 2

Sulfenyl thiocyanates

Benzenesulfenyl thiocyanate, C_6H_5SSCN	Colorless crystals of pungent odor. Liquefy when removed from ice–salt bath. Could not be distilled without decomposition. Prepared from thiophenol and thiocyanogen (1:2 molar ratio) in absolute ether. Yield not stated (63, 67).
2,4-Dinitrobenzenesulfenyl thiocyanate, $(NO_2)_2C_6H_3SSCN$	Yellow crystals. M.p. 74.5–76°C. From 2, 4-dinitrobenzenesulfenyl chloride and potassium thiocyanate, by shaking for 20 hr. at room temperature, in high yield (59).
Ethanesulfenyl thiocyanate, C_2H_5SSCN	Colorless liquid. B.p. 52°C./1.5 mm., with some decomposition. Possesses strong irritating odor. From 0.06 mole of thiocyanogen and 0.05 mole of ethyl mercaptan in ether. Yield, 50–60 per cent. Density > 1. Immiscible with water; soluble in ether. Dissolves in alcohol with liberation of cyanic acid (67).
2-Naphthalenesulfenyl thiocyanate, $C_{10}H_7SSCN$	Pale yellow crystals. M.p. 64.5–65°C. Odorless. From thiocyanogen and 2-mercaptonaphthalene (2:1 molar ratio) in ether solution. Insoluble in water; readily soluble in non-polar solvents (67, 87).
2-Nitrobenzenesulfenyl thiocyanate, $NO_2C_6H_4SSCN$	Yellow crystals from carbon tetrachloride. M.p. 93–94°C. From 2-nitrobenzenesulfenyl chloride and equivalent quantity of potassium thiocyanate, in benzene, by shaking for 20 hr. at room temperature. Quantitative yield (66). Also from *o*-nitrothiophenol and thiocyanogen; 75 per cent yield (67). Soluble in benzene and ethyl acetate; difficultly soluble in ether, ligroin, and carbon tetrachloride.

In many respects, the sulfenyl thiocyanates resemble the sulfenyl halides in chemical behavior.

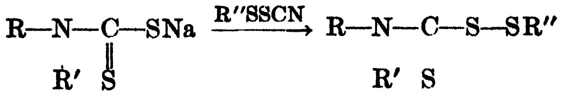
(*1*) By reactions with mercaptans and thiophenols a considerable number of disulfides have been prepared (66, 67).

(*2*) The reaction with an excess of ammonia or amines leads to sulfenamides. Thus, 2-nitrobenzenesulfenyl thiocyanate reacted with ammonia to give a quantitative yield of 2-nitrobenzenesulfenamide (66). Similarly, benzenesulfenyl thiocyanate reacted with diethylamine to give a 70 per cent yield of the corresponding diethylamide (63). The amides thus obtained were identical with the ones prepared from the corresponding sulfenyl chlorides (63, 108). Reactions of this type confirm the structure RSSCN for the sulfenyl thiocyanates. If these compounds were derivatives of isothiocyanic acid (HNCS), reaction with ammonia and amines would be expected to lead to derivatives of thiourea ($RSNHCSNH_2$).

(*3*) With dimethylaniline, 2-nitrobenzenesulfenyl thiocyanate reacted in the same manner as the sulfenyl chloride to give 4-dimethylaminophenyl 2-nitrophenyl sulfide (66).

(*4*) In the reaction of 2-nitrobenzenesulfenyl thiocyanate with potassium hydroxide solution, there was formed the same characteristic color as was observed in the case of the corresponding sulfenyl chloride (109). In both instances, it was presumed that the salt of the sulfenic acid was formed as an intermediate product, but the products of alkaline hydrolysis of the thiocyanate were not further described.

(*5*) In a recent patent (U.S. 2,390,713; December 11, 1945) Hunt describes the reaction of aliphatic sulfenyl thiocyanates with alkali metal salts of *N*-substituted dithiocarbamates to form sulfenyl derivatives, as shown below:



$$\mathrm{R{-}\underset{R'}{\underset{|}{N}}{-}\underset{S}{\underset{\|}{C}}{-}SNa \xrightarrow{R''SSCN} R{-}\underset{R'}{N}{-}\underset{S}{C}{-}S{-}SR''}$$

(*6*) 2-Nitrobenzenesulfenyl thiocyanate and 2,4-dinitrobenzenesulfenyl thiocyanate react with acetone or acetophenone to give the corresponding acetonyl or phenacyl aryl sulfides (*cf.* Section III, D, 3, (c) on page 294 for the corresponding reactions of sulfenyl halides).

Examples of reactions such as the above are, to be sure, restricted in number. The analogy to the sulfenyl halides, nevertheless, is rather clear. Lecher and coworkers were convinced of this relationship and of the correctness of classifying the sulfenyl thiocyanates as derivatives of sulfenic acids rather than as disulfides. In contrast to ordinary disulfides, they considered the sulfur-to-sulfur linkage in RS—SCN to be of a polar nature and even attempted to establish a tendency for ionic dissociation. However, 2-nitrobenzenesulfenyl thiocyanate proved to be a non-conductor of electricity in liquid sulfur dioxide solution (66).

A few differences in the properties of the sulfenyl halides and the sulfenyl thiocyanates have been noted, mainly in the greater hydrolytic stability which the latter compounds display in contrast, for example, to the sulfenyl chlorides. In their thermal stabilities they appear to be quite comparable to the sulfenyl chlorides. The hydrolytic stabilities toward water and alcohol vary widely, depending on the particular thiocyanate. Ethanesulfenyl thiocyanate was slowly hydrolyzed by cold water, and rapidly by hot water or alcohol. 2-Naphthalenesulfenyl thiocyanate was hydrolyzed very slowly by cold water, but was decomposed more rapidly by hot water or alcohol. 2-Nitrobenzenesulfenyl thiocyanate was found to be very indifferent to the action of water (66), whereas the analogous sulfenyl chloride underwent complete hydrolysis under comparable conditions (109). A study to extend the chemistry of sulfenyl thiocyanates, and particularly the reactions of these substances with olefins, is now in progress in the laboratories of the authors (59).

V. SULFENAMIDES

A considerable literature dealing with sulfenamides has been developed. Industrial investigators have been interested in these substances primarily because of their utility as accelerators for the vulcanization of rubber. Articles in the general literature have as their central interests the preparation of the sulfenamides and the study of their chemical properties. In this paper, references to the patent literature concerned with the applications of sulfenamides as rubber accelerators have been collected, and the contributions made to sulfenamide chemistry by these efforts have been noted. A discussion of the uses of sulfenamides in the manufacture of rubber, however, will not be undertaken.

A. TABULATION OF SULFENAMIDES

Table 3 lists the sulfenamides which were encountered in the course of this literature survey. The number of these which have been definitely characterized and recorded in the literature decidedly exceeds that of the sulfenyl halides known with an equal degree of exactness. As was true also of the sulfenyl halides, however, there are several references which merely imply that certain sulfenamides were prepared, but give little or no specific information. It may also be noted that the experimental studies cited in the patent literature are primarily concerned with the sulfenamides obtainable from 2-mercaptobenzothiazole and amines such as cyclohexylamine, butylamines, and piperidine. These sulfenamides have been found to be especially effective as accelerators for the vulcanization of rubber.

The sulfenamides have been designated in various ways: as sulfamines, sulfur amines, mercaptoamines, aminothio compounds, amino sulfides, sulfur amides, and thiohydroxylamines. The most convenient system of denoting these compounds would seem to be the one which considers them as derivatives of sulfenic acids. The names should be chosen in the same way as for sulfonamides, but the prefix "sulfon" should be changed to "sulfen." The examples in table 3 illustrate this nomenclature.

B. PREPARATION OF SULFENAMIDES

1. Sulfenamides from sulfenyl halides

The earliest instances of the preparation of sulfenamides were reported in the original papers of Zincke, who showed that the reaction of aromatic sulfenyl

TABLE 3

Sulfenamides

4-Acetamidobenzenesulfen(2-pyridylamide), $C_{13}H_{13}ON_3S$	Not isolated. From 4-acetamidobenzenesulfenyl chloride or bromide and 2-pyridylamine in inert solvents. Oxidized to corresponding sulfonamide (6a, 8).
4-Acetamidobenzenesulfen(4,6-dimethyl-2-pyrimidylamide), $C_{14}H_{16}ON_4S$	White powder. From the sulfenyl halide and amine in benzene (6b).
4-Acetamidobenzenesulfenoguanidide, $C_9H_{11}ON_3S$	Not isolated. Oxidized to the sulfonamide. From 4-acetamidobenzenesulfenyl chloride and guanidine nitrate in presence of sodium ethoxide, in ether at room temperature (6).
4-Amino-1-anthraquinonesulfenanilide, $C_{20}H_{14}O_2N_2S$	Violet-red needles. M.p. 180°C. (decomposition). From 4-amino-1-anthraquinonesulfenyl bromide hydrobromide and aniline in benzene solution (33).
2-Aminobenzenesulfenopiperidide, $C_{11}H_{16}N_2S$	Well-shaped crystals. M.p. 66–68°C. From 2-aminophenyl disulfide and piperidine with aqueous sodium hypochlorite in presence of excess pyridine at 50°C. (99).
1-Anthraquinonesulfenamide, $C_{14}H_9O_2NS$	Orange needles. Color lightens at 215°C., but solid does not melt even at 300°C. From the sulfenyl bromide and alcoholic ammonia (32).
1-Anthraquinonesulfenanilide, $C_{20}H_{13}O_2NS$	Red needles. M.p. 210°C. From the sulfenyl bromide and aniline in benzene (32).
2-Anthraquinonesulfenanilide, $C_{20}H_{13}O_2NS$	Orange needles from methyl alcohol. M.p. 171°C. From the sulfenyl chloride and aniline (32).
Benzenediazo triphenylmethyl sulfide, $(C_6H_5)_3CSN{=}NC_6H_5$	Yellow leaves. M.p. 108°C. (decomposition). From benzenediazonium chloride and triphenylmethylthiol (100).
Benzenesulfenanilide, $C_{12}H_{11}NS$	Colorless crystals. M.p. 53–55°C. From benzenesulfenyl chloride and aniline in ether (64).
Benzenesulfenodiethylamide, $C_{10}H_{15}NS$	Colorless liquid. B.p. 90°C./3.5 mm.; 94–96°C./5 mm. From benzenesulfenyl thiocyanate and diethylamine (70 per cent yield), or from the sulfenyl chloride (76 per cent yield) (63). Also from the sulfenyl bromide (64).
Benzenesulfenodimethylamide, $C_8H_{11}NS$	B.p. 63.5–64°C./3 mm. From benzenesulfenyl chloride and dimethylamine in absolute ether. Yield, 92 per cent (64).
Benzenesulfen(4,6-dimethyl-2-pyrimidylamide), $C_{12}H_{13}N_3S$	From benzenesulfenyl chloride and 4,6-dimethyl-2-pyrimidylamine. Crystals from alcohol. Oxidized to the sulfonamide (6b).

TABLE 3—*Continued*

Benzenesulfenoguanidide, $C_7H_9N_3S$	From the sulfenyl chloride, guanidine nitrate, and sodium ethoxide in dry benzene. Converted to the sulfonamide (6).
Benzenesulfen(2-pyridylamide), $C_{11}H_{10}N_2S$	Crystals from alcohol. Prepared from the sulfenyl chloride and 2-pyridylamine (6a).
2-Benzimidazolesulfenopiperidide, $C_{12}H_{15}N_3S$	M.p. 190–193°C. From 2-mercaptobenzimidazole and piperidine, with aqueous sodium hypochlorite (99).
2-Benzothiazolesulfenamide, $C_7H_6N_2S_2$	M.p. 128–129°C. From 2-mercaptobenzothiazole and cold concentrated aqueous ammonia with sodium hypochlorite, or from sodium 2-mercaptobenzothiazole and chloroamine at 0–5°C. Nearly quantitative yields (17, 18, 47).
2-Benzothiazolesulfen(2-aminoethylamide), $C_9H_{11}N_3S_2$	M.p. 122–123°C. From 2-benzothiazolesulfenamide and ethylenediamine (53). From the mercaptan and amine with aqueous hypochlorite; white powder, m.p. 115°C. (1, 17, 18).
2-Benzothiazolesulfenanilide, $C_{13}H_{10}M_2S_2$	M.p. 119–122°C. From the sulfenyl chloride and amine (70).
2-Benzothiazolesulfenobenzylamide, $C_{14}H_{21}N_2S_2$	M.p. 115°C. From 2-mercaptobenzothiazole and benzylamine with aqueous sodium hypochlorite (18). From 2-benzothiazolesulfenamide and benzylamine, m.p. 111–114°C. (53).
2-Benzothiazolesulfenobenzylmethylamide, $C_{15}H_{14}N_2S_2$	From the mercaptan and amine with aqueous hypochlorite; about 85 per cent yield (99).
2-Benzothiazolesulfenobutylamide, $C_{11}H_{16}N_2S_2$	Red oil. From sodium 2-mercaptobenzothiazole and butylamine with aqueous hypochlorite, about 85 per cent yield (1).
2-Benzothiazolesulfen-*sec*-butylamide, $C_{11}H_{14}N_2S_2$	White. M.p. 59–61°C. (1, 22, 94).
2-Benzothiazolesulfenocyclohexylamide, $C_{13}H_{16}N_2S_2$	M.p. 99–101°C. (1, 18, 22, 48, 53).
2-Benzothiazolesulfen(2-cyclohexylcyclohexylamide), $C_{19}H_{26}N_2S_2$	Waxy, buff-colored solid (22).
2-Benzothiazolesulfeno(dibutylamide), $C_{15}H_{22}N_2S_2$	Oil. From 2-benzothiazolesulfenamide and dibutylamine (53), or from 2-mercaptobenzothiazole and the amine with sdium hypochlorite, 70 per cent yield (99).

TABLE 3—*Continued*

2-Benzothiazolesulfeno(diethylamide), $C_{11}H_{14}N_2S_2$	Oil. Prepared in same ways as the dibutyl derivative (53, 99).
2-Benzothiazolesulfeno(dipropylamide), $C_{13}H_{18}N_2S_2$	Oil. From 2-benzothiazolesulfenamide and dipropylamine (53).
2-Benzothiazolesulfenethylamide, $C_9H_{10}N_2S_2$	White. M.p. 52–53°C. (53); m.p. 55–57°C. (17).
2-Benzothiazolesulfen(2-hydroxyethylamide), $C_9H_{10}ON_2S_2$	M.p. 96–99°C. (1, 22).
2-Benzothiazolesulfen(isopropylamide), $C_{10}H_{12}N_2S_2$	White crystals. M.p. 93–94°C. (53, 94).
2-Benzothiazolesulfenomethylamide, $C_8H_8N_2S_2$	Amber liquid or low-melting solid (17, 22).
2-Benzothiazolesulfen(1-methylbutylamide), $C_{12}H_{16}N_2S_2$	White solid. M.p. 58–60°C. From sodium 2-mercaptobenzothiazole and 1-methylbutylamine, with sodium hypoiodite, in good yield (94).
2-Benzothiazolesulfen(1-methylisopentylamide), $C_{13}H_{18}N_2S_2$	White. M.p. 52–64°C. (94).
2-Benzothiazolesulfenomorpholide, $C_{11}H_{12}ON_2S_2$	M.p. 86–87°C. From 2-benzothiazolesulfenamide and morpholine (53).
2-Benzothiazolesulfen(*N*-ethylcyclohexylamide), $C_{15}H_{20}N_2S_2$	Oil (99).
2-Benzothiazolesulfenopentylamide, $C_{12}H_{16}N_2S_2$	White. M.p. 35–37°C. (1, 17).
2-Benzothiazolesulfen-*tert*-pentylamide, $C_{12}H_{16}N_2S_2$	M.p. 80–82°C. (94).
2-Benzothiazolesulfenopiperidide, $C_{12}H_{14}N_2S_2$	White crystals. M.p. 80°C. Obtained by various oxidative methods from the mercaptan and amine (1, 53, 99).
2-Benzothiazolesulfenopropylamide, $C_{10}H_{12}N_2S_2$	White. M.p. 32–33°C. (17).
Bis(benzenesulfen)imide, $C_6H_5SNHSC_6H_5$	Colorless, odorless crystals. Melt with evolution of ammonia at 126.5–128°C. (corr.). From ammonia and excess benzenesulfenyl chloride, in ether. Poor yield (64).
Bis(1-chloro-2-naphthalenesulfeno)methylimide, $C_{21}H_{15}NS_2Cl_2$	Shiny leaves from benzene-petroleum ether. M.p. 177–178°C. (108).

TABLE 3—*Continued*

Bis(4-chloro-2-nitrobenzenesulfen)-imide, $C_{12}H_7O_4N_3S_2Cl_2$	Pale yellow needles. M.p. 210°C. (decomposition) (106).
Bis(4-chloro-2-nitrobenzenesulfen)-*o*-phenylenediamide, $C_{18}H_{12}O_4N_4S_2Cl_2$	M.p. 181°C. From 4-chloro-2-nitrobenzenesulfenyl chloride and *o*-phenylenediamine in ether, 2:1 molar ratio (40).
Bis(4-chloro-2-nitrobenzenesulfen)-*m*-phenylenediamide	Brown-red powder. Decomposes at 70–80°C. (41).
Bis(4-chloro-2-nitrobenzenesulfen)-*p*-phenylenediamide	M.p. 212°C. (40).
Bis(4-methyl-2-nitrobenzenesulfen)-imide, $C_{14}H_{13}O_4N_3S_2$	Yellow needles. M.p. 241°C. From 4-methyl-2-nitrobenzenesulfenamide by boiling with acetic acid (114).
Bis(4-methyl-2-nitrobenzenesulfeno)methylimide, $C_{15}H_{15}O_4N_3S_2$	Yellow crystals. M.p. 226°C. (decomposition). From 4-methyl-2-nitrobenzenesulfenomethylamide by heating with acetic acid (114).
Bis(2-nitrobenzenesulfen)imide, $C_{12}H_9O_4N_3S_2$	Lemon-yellow needles or powder. M.p. 217°C. (decomposition). From the amide by boiling with dilute acetic acid, or from the sulfenyl chloride and dilute aqueous ammonia (109).
Bis(4-nitrobenzenesulfen)imide, $O_2NC_6H_4SNHSC_6H_4NO_2$	Pale yellow needles. M.p. 155°C. From ammonia and excess 4-nitrobenzenesulfenyl chloride, or more simply by boiling the corresponding amide with dilute acetic acid (113).
Bis(2-nitrobenzenesulfeno)methylimide, $C_{13}H_{11}O_4N_3S_2$	Yellow. M.p. 204–5°C. (decomposition). Prepared in same manner as the corresponding sulfenimide above (109).
Bis(4-nitrobenzenesulfeno)methylimide, $C_{13}H_{11}O_4N_3S_2$	Pale yellow needles from glacial acetic acid. M.p. 156°C. (113).
Bis(*p*-toluenesulfen)imide, $CH_3C_6H_4SNHSC_6H_4CH_3$	Could not be obtained pure; very unstable. From *p*-toluenesulfenyl chloride and ammonia (64).
4-Chlorobenzenesulfen(4,6-dimethyl-2-pyrimidylamide), $C_{12}H_{12}N_3SCl$	From the sulfenyl chloride and the amine, in benzene at room temperature. Recrystallized from alcohol (6b).
4-Chlorobenzenesulfenoguanidide, $C_7H_8N_2SCl$	Not isolated. From the sulfenyl chloride and guanidine nitrate with sodium ethoxide in benzene. Oxidized to sulfonamide (6).
4-Chlorobenzenesulfen(2-pyridylamide), $C_7H_8N_3SCl$	Not isolated; oxidized to sulfonamide (6a).

TABLE 3—*Continued*

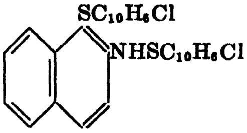
1-Chloro-2-naphthalenesulfenamide, $C_{10}H_8NSCl$	Needles which easily turn to red color. Melt at about 160°C. with previous decomposition at about 105–110°C. (108).
1-Chloro-2-naphthalenesulfenanilide, $C_6H_{12}NSCl$	M.p. 132°C. From the sulfenyl chloride and aniline, 1:2 molar ratio (108).
Bis(1-chloro-2-naphthalenesulfen)-imide, $C_{20}H_{13}NS_2Cl_2$	Red, flocculent crystals. M.p. 213–214°C. From 1-chloro-2-naphthalenesulfenamide by treatment with cold acetic acid or by action of excess ammonia and the sulfenyl chloride (108).
1-Chloro-2-naphthalene(1-(1-chloro-2-naphthylthio)2-naphthylamide)  	Nearly colorless needles. M.p. 187–188°C. From 1-chloro-2-naphthalenesulfenyl chloride and 1-chloro-2-naphthylthio(2-naphthylamine) in 1:2 molar ratio (108).
1-Chloro-2-naphthalenesulfenomethylamide, $C_{11}H_{10}NSCl$	Leaves from aqueous methyl alcohol. M.p. 89–90°C. (108).
1-Chloro-2-naphthalenesulfen-α-naphthylamide, $C_{20}H_{14}NSCl$	M.p. 154°C. From the sulfenyl chloride and α-naphthylamine (108).
1-Chloro-2-naphthalenesulfen-β-naphthylamide	Colorless needles. M.p. 132–133°C. (108).
4-Chloro-2-nitrobenzenesulfenamide, $C_6H_5O_2N_2SCl$	Bright yellow needles. M.p. 126–127°C. From the sulfenyl chloride and ammonia in cold chloroform solution. Converted to an acetyl derivative (106).
4-Chloro-2-nitrobenzenesulfenanilide $C_{12}H_9O_2N_2SCl$	Orange-yellow crystals from alcohol. M.p. 102°C. From the sulfenyl chloride and aniline in ether (76); m.p. 100°C. (42).
4-Chloro-2-nitrobenzenesulfen-*o*-chloroanilide, $C_{12}H_8O_2N_2SCl_2$	Orange needles. M.p. 112°C. From the sulfenyl chloride and *o*-chloroaniline (42, 77).
4-Chloro-2-nitrobenzenesulfen-*p*-chloroanilide	Brown-red crystals. M.p. 172°C. (41).
4-Chloro-2-nitrobenzenesulfen(2,4-dichloroanilide), $C_{12}H_7O_2N_2SCl_3$	Golden yellow needles. M.p. 154°C. (41).
4-Chloro-2-nitrobenzenesulfen(2,4-dihydroxyanilide), $C_{12}H_9O_4N_2SCl$	Poorly crystalline. Appeared to melt at 133°C. From the sulfenyl chloride and 2,4-dihydroxyaniline (38).
4-Chloro-2-nitrobenzenesulfen-*p*-dimethylaminoanilide, $C_{14}H_{14}O_2N_3SCl$	Crystals from ether. M.p. 152°C. (40).

TABLE 3—*Continued*

4-Chloro-2-nitrobenzenesulfenodiphenylamide, $C_{18}H_{13}O_2N_2SCl$	M.p. 127°C. (42). Compare 2-nitrobenzenesulfenodiphenylamide (below).
4-Chloro-2-nitrobenzenesulfen-*p*-ethoxyanilide, $C_{14}H_{13}O_3N_2SCl$	Red crystals. M.p. 86°C. From the sulfenyl chloride and *p*-phenetidine.
4-Chloro-2-nitrobenzenesulfenethylanilide, $C_{14}H_{13}O_2N_2SCl$	Red crystals. M.p. 74°C. (41).
4-Chloro-2-nitrobenzenesulfen-*o*-hydroxyanilide, $C_{12}H_9O_3N_2SCl$	Red-brown crystals. M.p. 143°C. From the sulfenyl chloride and *o*-aminophenol in ether (40).
4-Chloro-2-nitrobenzenesulfen-*p*-hydroxyanilide	Red leaves from benzene. M.p. 118–119°C. (38, 39).
4-Chloro-2-nitrobenzenesulfenomethylanilide, $C_{13}H_{11}O_2N_2SCl$	Orange-red. Did not crystallize well, but analyzed correctly (37).
4-Chloro-2-nitrobenzenesulfen-α-naphthylamide, $C_{16}H_{11}O_2N_2SCl$	Red crystals. M.p. 180°C. (41).
4-Chloro-2-nitrobenzenesulfen-β-naphthylamide	Brown-red crystals. M.p. 176°C. (41).
4-Chloro-2-nitrobenzenesulfen(*p*-phenylazoanilide), $ClNO_2C_6H_3SNHC_6H_4N{=}NC_6H_5$	Red crystals from ether. M.p. 188°C. From the sulfenyl chloride and aminoazobenzene (37).
4-Chloro-2-nitrobenzenesulfen-*o*-toluidide, $C_{13}H_{11}O_2N_2SCl$	Orange-red plates from alcohol. M.p. 127°C. (76); pale yellow crystals, m.p. 123°C. (41).
4-Chloro-2-nitrobenzenesulfen-*p*-toluidide	Red crystals. M.p. 137°C. (41).
4-Chloro-2-nitrobenzenesulfen(2,4,6-trimethylanilide), $C_{15}H_{15}O_2N_2SCl$	Golden yellow needles. M.p. 178°C. (41).
2,5-Dichlorobenzenesulfenanilide, $C_{12}H_9NSCl_2$	White needles. M.p. 85°C. (37).
2,4-Dinitrobenzenesulfenanilide, $C_{12}H_9O_4N_3S$	M.p. 142.5–143°C. (14). This compound and the other 2,4-dinitrobenzenesulfenamides listed below were prepared from the sulfenyl chloride and amines in ether solution.
2,4-Dinitrobenzenesulfenobutylamide, $C_{10}H_{13}O_4N_3S$	M.p. 88.5–89°C. (14).
2,4-Dinitrobenzenesulfen-*p*-bromoanilide, $C_{12}H_8O_4N_3SBr$	M.p. 180.5–181°C. (14).
2,4-Dinitrobenzenesulfen-*p*-chloroanilide, $C_{12}H_8O_4N_3SCl$	M.p. 164–164.5°C. (14).

TABLE 3—*Continued*

2,4-Dinitrobenzenesulfenocyclohexylamide, $C_{12}H_{15}O_4N_3S$	M.p. 109.5–110°C. (14).
2,4-Dinitrobenzenesulfen(*N*-cyclohexylmethylamide), $C_{13}H_{17}O_4N_3S$	M.p. 95.5–96°C. (14).
2,4-Dinitrobenzenesulfenethylamide, $C_8H_9O_4N_3S$	M.p. 66–66.5°C. (14).
2,4-Dinitrobenzenesulfenomethylamide, $C_7H_7O_4N_3S$	M.p. 99–99.5°C. (14).
2,4-Dinitrobenzenesulfen-*p*-methoxy anilide, $C_{13}H_{11}O_5N_3S$	M.p. 158–159°C. (14).
2,4-Dinitrobenzenesulfen-*α*-naphthylamide, $C_{16}H_{11}O_4N_3S$	M.p. 188.5–189°C. (14).
2,4-Dinitrobenzenesulfen-*β*-naphthylamide	M.p. 167–168°C. (14).
2,4-Dinitrobenzenesulfenopentylamide, $C_{11}H_{15}O_4N_3S$	Oil (14).
2,4-Dinitrobenzenesulfenopropylamide, $C_9H_{11}O_4N_3S$	M.p. 94–94.5°C. (14).
2,4-Dinitrobenzenesulfen-*o*-toluidide $C_{13}H_{11}O_4N_3S$	M.p. 155–156°C. (14).
2,4-Dinitrobenzenesulfen-*p*-toluidide	M.p. 161–161.5°C. (14).
2-Methyl-2-butanesulfenopiperidide, $C_{10}H_{21}NS$	Colorless liquid. B.p. 100°C./12 mm. From the sulfenyl iodide and piperidine in ether (87).
4-Methyl-2-nitrobenzenesulfenamide, $C_7H_8O_2N_2S$	Orange-red needles. M.p. 147°C. Acetyl derivative, m.p. 188°C. (decomposition) (114).
4-Methyl-2-nitrobenzenesulfenanilide, $C_{13}H_{12}O_2N_2S$	Pale orange crystals. M.p. 91°C. (114).
4-Methyl-2-nitrobenzenesulfenodimethylamide, $C_9H_{12}O_2N_2S$	Yellow needles. M.p. 76°C. (114).
4-Methyl-2-nitrobenzenesulfenomethylamide, $C_8H_{10}O_2N_2S$	Deep yellow needles. M.p. 46°C. (114).
4-Methyl-2-nitrobenzenesulfenomethylanilide, $C_{14}H_{14}O_2N_2S$	Yellow crystals. M.p. 78°C. (114).
4-Methyl-2-nitrobenzenesulfen(1-(4-methyl-2-nitrophenylthio)-2-naphthylamide), $C_{24}H_{19}O_4N_3S_2$	Yellow-brown crusts. M.p. 184°C. (114).

TABLE 3—*Continued*

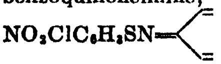
4-Methyl-2-nitrobenzenesulfen-α-naphthylamide, $C_{17}H_{14}O_2N_2S$	Pale orange needles. M.p. 143°C. (114).
4-Methyl-2-nitrobenzenesulfen-β-naphthylamide	Pale orange needles. M.p. 177°C. (114).
4-Methyl-2-nitrobenzenesulfen-*o*-toluidide, $C_{14}H_{14}O_2N_2S$	Brown-red plates or leaves. M.p. 140°C. (114).
4-Methyl-2-nitrobenzenesulfen-*p*-toluidide	Yellow-brown prisms. M.p. 81°C. (114).
N-Benzylidene-1-chloro-2-naphthalenesulfenamide, $ClC_{10}H_6SN{=}CHC_6H_5$	Colorless needles. M.p. 106–107°C. From 1-chloronaphthalene-2-sulfenamide and benzaldehyde in alcohol at room temperature for 24 hr. (108).
N-Benzylidene-4-chloro-2-nitrobenzenesulfenamide, $ClNO_2C_6H_3SN{=}CHC_6H_5$	Yellow needles. M.p. 161°C. From 4-chloro-2-nitrobenzenesulfenamide and benzaldehyde in boiling alcohol (106).
N-Benzylidene-4-methyl-2-nitrobenzenesulfenamide, $C_{14}H_{12}O_2N_2S$	Yellow needles. M.p. 146°C. (114).
N-Benzylidene-2-nitrobenzenesulfenamide, $C_{13}H_{10}O_2N_2S$	Golden yellow needles. M.p. 159°C. (109).
N-Benzylidene-4-nitrobenzenesulfenamide, $C_{13}H_{10}O_2N_2S$	Shining, silken needles. M.p. 130°C. (113).
N-Benzylidenetriphenylmethanesulfenamide, $C_{26}H_{21}NS$	Yellow needles. M.p. 128°C. From triphenylmethanesulfenamide and benzaldehyde in benzene in presence of sodium ethoxide (100).
N-(4-Chloro-2-nitrophenylthio)-*p*-benzoquinoneimine,  $NO_2ClC_6H_3SN{=}$	Orange crystals. M.p. 194°C. By oxidation of 4-chloro-2-nitrobenzenesulfen-*p*-hydroxyanilide with hydrogen peroxide (39).
N-(4-Chloro-2-nitrophenylthio)-2-hydroxy-*p*-benzoquinoneimine, $C_{12}H_7O_4N_2SCl$	By oxidation of 4-chloro-2-nitrobenzenesulfen(2,4-dihydroxyanilide) with hydrogen peroxide (38).
N-Isopropylidene-4-methyl-2-nitrobenzenesulfenamide, $CH_3NO_2C_6H_3SN{=}C(CH_3)_2$	Yellow needles. M.p. 116°C. From 4-methyl-2-nitrobenzenesulfenamide by refluxing with acetone (114).
N-Isopropylidene-2-nitrobenzenesulfenamide, $C_9H_{10}O_2N_2S$	Yellow needles. M.p. 86°C. (109).
2-Naphthoxazolesulfenopiperidide, $C_{16}H_{16}ON_2S$	Crystals from alcohol. M.p. 71–73°C. From 2-mercaptonaphthoxazole and piperidine with aqueous sodium hypochlorite (99).

TABLE 3—*Continued*

2-Nitrobenzenesulfenamide, $C_6H_6O_2N_2S$	Golden needles. M.p. 124–125°C. Acetyl derivative, m.p. 179°C. From the sulfenyl chloride and ammonia in ether (15, 109); or from 2-nitrobenzenesulfenyl thiocyanate and ammonia in benzene (66).
2-Nitrobenzenesulfenanilide, $C_{12}H_{10}O_2N_2S$	Brick-red crystals. M.p. 95°C. (74); m.p. 94°C. (109); 88.5–89°C. (corr.) (15).
2-Nitrobenzenesulfenobutylamide, $C_{10}H_{14}O_2N_2S$	M.p. 27–28°C. (corr.) (15).
2-Nitrobenzenesulfen-*p*-bromoanilide, $C_{12}H_9O_2N_2SBr$	M.p. 146–146.5°C. (corr.) (15).
2-Nitrobenzenesulfen-*o*-chloroanilide, $C_{12}H_9O_2N_2SCl$	Crystals from alcohol. M.p. 130°C. (56, 76).
2-Nitrobenzenesulfen-*p*-chloroanilide	M.p. 143.5–144°C. (corr.) (15).
2-Nitrobenzenesulfenocyclohexylamide, $C_{12}H_{16}O_2N_2S$	M.p. 51.5–52°C. (corr.) (15).
2-Nitrobenzenesulfenodiethylamide, $C_{10}H_{14}O_2N_2S$	Oil (15).
2-Nitrobenzenesulfenodimethylamide, $C_8H_{10}O_2N_2S$	Yellow leaves or needles from methyl alcohol. M.p. 62.5–63°C. (corr.) (15); 63°C. (109).
2-Nitrobenzenesulfenodiphenylamide, $C_{18}H_{14}O_2N_2S$	Could not be prepared from the sulfenyl chloride and diphenylamine (15).
2-Nitrobenzenesulfenethylamide, $C_8H_{10}O_2N_2S$	M.p. 32.5–33°C. (15).
2-Nitrobenzenesulfen-4-methoxyanilide, $C_{13}H_{12}O_3N_2S$	M.p. 138–138.5°C. (corr.) (15).
2-Nitrobenzenesulfenomethylamide, $C_7H_8O_2N_2S$	Deep yellow needles. M.p. 36°C. (15, 109).
2-Nitrobenzenesulfenomethylanilide, $C_{13}H_{12}O_2N_2S$	M.p. 86–86.5°C. (corr.) (15).
2-Nitrobenzenesulfen-*o*-nitroanilide, $C_{12}H_9O_4N_3S$	Could not be prepared from the sulfenyl chloride and *o*-nitroaniline (15).
2-Nitrobenzenesulfen-*α*-naphthylamide, $C_{16}H_{12}O_2N_2S$	M.p. 130.5–131°C. (corr.) (15); 129°C. (109).
2-Nitrobenzenesulfen-*β*-naphthylamide, $C_{16}H_{12}O_2N_2S$	M.p. 202–202.5°C. (corr.) (15); 188°C. (109).

TABLE 3—*Continued*

2-Nitrobenzenesulfen-(1-(2-nitrophenylthio)-2-naphthylamide), $C_{22}H_{15}O_4N_3S_2$	Yellow crystals. M.p. 186–187°C. (109).
2-Nitrobenzenesulfenopropylamide, $C_9H_{12}O_2N_2S$	Oil (15).
2-Nitrobenzenesulfen-*o*-toluidide, $C_{13}H_{12}O_2N_2S$	Reddish orange crystals. M.p. 119.5–120°C. (74); 115.5–116°C. (corr.) (15).
2-Nitrobenzenesulfen-*m*-toluidide	M.p. 106.5–107°C. (15).
2-Nitrobenzenesulfen-*p*-toluidide	Golden yellow needles or leaves. M.p. 136–136.5°C. (corr.) (15); 135°C. (74); 133°C. (109).
4-Nitrobenzenesulfen(2-benzothiazolylamide), $C_{13}H_9O_2N_3S_2$	Yellow needles. M.p. 193°C. From 4-nitrobenzenesulfenyl chloride and 2-benzothiazolylamine (8).
4-Nitrobenzenesulfenamide, $C_6H_6O_2N_2S$	Deep yellow needles. M.p. 103°C. (113).
4-Nitrobenzenesulfenanilide, $C_{12}H_{10}O_2N_2S$	Yellow leaves or needles. M.p. 75°C. (74, 113).
4-Nitrobenzenesulfen-*o*-chloroanilide, $C_{12}H_9O_2N_2SCl$	Crystals from alcohol. M.p. 99–101°C. (76).
4-Nitrobenzenesulfenodimethylamide, $C_8H_{10}O_2N_2S$	Yellow. M.p. 48°C. (113).
4-Nitrobenzenesulfen(4,6-dimethyl-2-pyrimidylamide), $C_{12}H_{12}O_2N_4S$	Crystals from alcohol. From ethyl 4-nitrobenzenesulfenate and the amine in dry benzene. Oxidized to the sulfonamide (6b).
4-Nitrobenzenesulfenoguanidide, $C_7H_8O_2N_4S$	Not isolated. Oxidized to the sulfonamide. From ethyl 4-nitrobenzenesulfenate or the corresponding sulfenyl chloride plus guanidine nitrate and sodium ethoxide in benzene (6).
4-Nitrobenzenesulfenomethylamide, $C_7H_8O_2N_2S$	Yellow needles. M.p. 48°C. (113).
4-Nitrobenzenesulfen(4-methyl-2-thiazolylamide), $C_{10}H_9O_2N_3S_2$	Not isolated; used in synthesis (6c).
4-Nitrobenzenesulfen(4-methyl-2-thiazolylmethylamide), $C_{11}H_{11}O_2N_3S_2$	Not isolated; used in synthesis. From the sulfenyl chloride and *N*-methyl(4-methyl-2-thiazolylamine) (5).
4-Nitrobenzenesulfen(1-(4-nitrophenylthio)-2-naphthylamide), $C_{22}H_{15}O_4N_3S_2$	Yellow crystals. M.p. 195°C. (113).

TABLE 3—*Concluded*

4-Nitrobenzenesulfen(2-pyridylamide), $C_{11}H_9O_2N_3S$	Prisms from benzene. M.p. 170–173°C. From the sulfenyl chloride or ethyl sulfenate and 2-pyridylamine (6a, 8).
4-Nitrobenzenesulfen(2-pyrimidylamide), $C_{10}H_8O_2N_4S$	Not isolated. Oxidized to the corresponding sulfonamide (6b).
4-Nitrobenzenesulfen-*p*-toluidide, $C_{13}H_{12}O_2N_2S$	Yellow needles. M.p. 73°C. (113).
N,*N'*-(Bis-4-chloro-2-nitrobenzenesulfenyl)benzidine, $(ClNO_2C_6H_3SNHC_6H_4)_2$	M.p. 235°C. (decomposition) (42).
N,*N*-Bis(trimethylmethanesulfenyl)piperazine, $C_{12}H_{26}N_2S_2$	Colorless leaves. M.p. 120°C. From the sulfenyl chloride, bromide, or iodide plus piperazine in ether (85, 87).
p-Toluenesulfenanilide, $C_{13}H_{13}NS$	Colorless needles. M.p. 80–81°C. (64, 65).
Trimethylmethanesulfenodimethylamide, $C_6H_{15}NS$	B.p. 55.5°C./82 mm.; 58.5°C./90 mm.; 60.5°C./96 mm.; 47–51 per cent yield from the sulfenyl iodide and amine (87).
Trimethylmethanesulfenomethylamide, $C_5H_{13}NS$	Colorless liquid of amine-like odor. B.p. 56.5°C./58 mm.; 61.5°C./70 mm.; 65°C./80 mm.; 68.5°C./94 mm.; 54–56 per cent yield (87).
Triphenylmethanesulfenamide, $C_{19}H_{17}NS$	Colorless crystals. M.p. 126°C. Acetyl derivative, m.p. 187°C. (100).
Triphenylmethanesulfenanilide, $C_{25}H_{21}NS$	White plates. M.p. 103°C. (100).
Triphenylmethanesulfenodimethylamide, $C_{21}H_{21}NS$	Colorless leaves. M.p. 105–108°C. (100).
Triphenylmethanesulfenomethylamide, $C_{20}H_{19}NS$	Colorless leaves from chloroform–alcohol. M.p. 119–120°C. Acetyl derivative, m.p. 133°C.; *N*-nitroso derivative, m.p. 102–103°C. (100).
Triphenylmethanesulfen-*o*-toluidide, $C_{26}H_{23}NS$	Crystals from toluene. M.p. 141°C. (100).

halides with ammonia and primary or secondary amines provided a general method for the preparation of the corresponding sulfenamides.

$$RSX + 2HNR_2 \rightarrow RSNR_2 + R_2NH_2X \qquad (49)$$

This method has been used for the synthesis of a variety of sulfenamides (see table 3). The formation of the sulfenamide is generally achieved by adding ammonia or the amine to the sulfenyl halide dissolved in ether or another appropriate solvent. The hydrogen halide generated in the reaction may be conveniently removed by the use of an excess of the reacting amine. The yields of sulfenamides obtainable by this method are usually reported to be high. The reactions proceed smoothly, at low temperatures, and usually occur spontaneously. However, not all amines react with equal facility. Thus, Billman and O'Mahony reported that weakly basic amines such as diphenylamine and *o*-nitroaniline did not react with 2-nitrobenzenesulfenyl chloride, whereas reaction with ammonia, aliphatic amines, aniline, *p*-anisidine, and *p*-bromoaniline occurred with ease (15). In boiling ether solution, however, Gebauer-Fülnegg found that 4-chloro-2-nitrobenzenesulfenyl chloride reacted with diphenylamine to give the expected sulfenamide (see table 3). He reported also that 2,4,6-trichloroaniline, 2,4,6-tribromoaniline, and 2,4-dichloro-1-naphthylamine did not react with 4-chloro-2-nitrobenzenesulfenyl chloride (41). If the sulfenyl halide is subject to hydrolysis, anhydrous conditions are required. However, with a sulfenyl halide such as 2-nitrobenzenesulfenyl chloride, which is not readily decomposed by water, the presence of hydroxylic solvents is not objectionable. As a matter of fact, the reaction of the above sulfenyl chloride with amines has been recommended as a method for identification of the latter in aqueous solutions (15).

2. Sulfenamides from mercaptans

A second procedure for the preparation of certain sulfenamides consists in the reaction between aromatic mercaptans and amines in the presence of oxidizing agents.

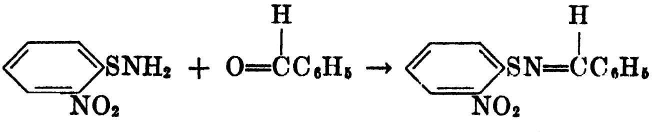
$$\text{ArSH} + \text{HNR}_2 \xrightarrow{(\text{O})} \text{ArSNR}_2 + \text{H}_2\text{O} \qquad (50)$$

Various modifications for effecting the oxidative elimination of hydrogen between compounds such as 2-mercaptobenzothiazoles and amines have been described in the patent literature (1, 17, 18, 22, 47, 48, 92, 94, 99, 103). Reagents such as hypochlorites, hydrogen peroxide, potassium persulfate, potassium ferricyanide, and the halogens have been reported to be useful for this purpose. However, the number of examples illustrating the application of these oxidizing agents in such reactions is definitely insufficient to permit sound evaluations of their relative efficiencies for the preparation of different types of sulfenamides. Such a comparative study of the synthesis of selected sulfenamides by various methods is now being made in the laboratories of the authors (58).

It is clear that in the synthesis of sulfenamides by reaction of thiophenols or mercaptans with amines in the presence of oxidizing agents, the main competing reaction is the formation of disulfides by oxidation of the thiol. The authors (58) have not been able to verify patent claims for the oxidative formation of sulfenamides, using hydrogen peroxide or potassium ferricyanide as oxidizing agents, with various combinations of thiols and amines. Disulfides were the only products isolated. The oxidative elimination of hydrogen between 2-mercaptobenzothiazole and aliphatic amines whose basicities are equal to or greater than that of ammonia has, however, been achieved by various workers (see references above) by employing mild alkaline conditions and aqueous solutions of hypochlorites as oxidizing agents. The method does not seem applicable to aliphatic mercaptans, in which case disulfide formation predominates. Thus, with benzyl mercaptan and various amines, benzyl disulfide was the only product isolated in yields of over 90 per cent (58). The preparation of sulfenamides from aromatic thiols and aromatic amines has been claimed in patents, but such claims still await confirmation.

3. Sulfenamides by other methods

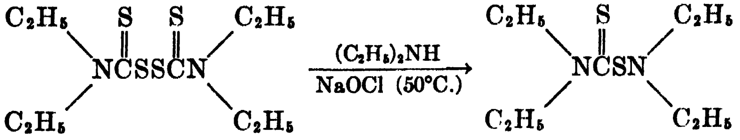
The reaction of sulfenyl thiocyanates with amines affords another synthetic approach to the sulfenamides, but its use has been demonstrated in only a few instances to date (see page 303). It has also been found that certain sulfenamides derived from ammonia react readily with aldehydes and ketones in a manner similar to the formation of Schiff bases from amines and carbonyl compounds. For example:



(51)

XXV

This reaction may therefore serve as a method of preparation for sulfenamides such as compound XXV. In the patent literature (103) it has also been indicated that disulfides such as 2-benzothiazolyl disulfide and aliphatic amines such as piperidine react at temperatures of from 40–150°C. to yield corresponding sulfenamides. It has also been reported that the reaction of tetraethylthiuram disulfide with diethylamine, in the presence of aqueous sodium hypochlorite, leads to the formation of the sulfenamide XXVI (99).



(52)

XXVI

Examples of the formation of the related sulfenimides have been noted on pages 299 and 319, and have been included in table 3.

The spontaneous displacement of the amino group from 2-benzothiazolesulfenamide by other amines whose base strengths are greater than that of ammonia has been reported in a recent patent (53). Thus, mixing 2-benzothiazolesulfenamide with cyclohexylamine results in the formation of 2-benzothiazolesulfenocyclohexylamide and ammonia. Similar reactions have been reported for 2-benzothiazolesulfenamide and ethylamine, ethylenediamine, isopropylamine, benzylamine, morpholine, piperidine, dipropylamine, and dibutylamine (see table 3). These displacement reactions permit the formation of certain types of sulfenamides and are also reminiscent of the displacement reactions observed in studies of the sulfenanilides (see page 322). It may also be pointed out that the synthesis of sulfenamides may be carried out by using the sulfenic acid esters in place of sulfenyl halides or thiocyanates. Thus, the reaction of 4-nitrobenzenesulfenyl chloride or of ethyl 4-nitrobenzenesulfenate with 2-pyridylamine leads to the same sulfenamide (see table 3).

C. PHYSICAL PROPERTIES OF SULFENAMIDES

The sulfenamides are generally crystalline substances, possessed of sharp melting points, although some members of low molecular weight are liquids. Nitro-substituted aromatic sulfenamides are always reported to be colored, but the sulfenamide group itself is not a chromophore. The solubilities of the sulfenamides vary with the nature of the substituents present, but as a rule, they are more soluble in non-polar solvents, such as benzene and chloroform, than they are in the more polar solvents. Specific physical properties are recorded in table 3.

D. CHEMICAL PROPERTIES OF SULFENAMIDES

1. Thermal stability

The sulfenamides display considerable thermal stability. They may be recrystallized unchanged from various solvents, and the liquid members may be purified by distillation at reduced pressures. When heated at 150–160°C. for several hours, some sulfenanilides rearrange to amino sulfides (see page 321).

2. Acylation

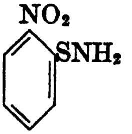
In some respects, the sulfenamides resemble amines rather than amides. The ease of formation of acetyl and benzoyl derivatives by conventional methods (85, 100, 109, 114) seems to be one instance in support of this observation. The reaction with carbonyl compounds (equation 51) is another example of this similarity to amines, as is also the formation of *N*-nitroso derivatives from an amide such as triphenylmethanesulfenamide (100).

3. Acidic and basic character

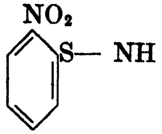
In contrast to sulfonamides, the sulfenamides do not display acidic character in aqueous solution. For example, it has been found that various 2-nitrobenzenesulfenamides are not soluble in 10 per cent aqueous sodium hydroxide solution (15). While the sulfenamides probably do possess weakly basic properties, these are not sufficient to allow the formation of salts such as hydrochlorides in aqueous solution. Acid solutions readily effect hydrolysis of the sulfenamide linkage, and it is likely that in this process, the first step is the coördination of the proton by the nitrogen atom of the sulfenamide linkage.

4. Hydrolytic scissions

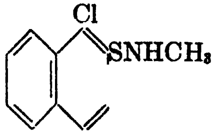
Billman and coworkers (14, 15) found that various 2-nitrobenzenesulfenamides were cleaved by the passage of hydrogen chloride, for 3 min., into their ethereal solutions. The corresponding sulfenyl halides and amine hydrochlorides were recovered in this procedure in nearly quantitative amounts. Hydrolytic cleavage of the sulfenamides has also been observed by other workers and has even been used to advantage in the synthesis of certain sulfenyl chlorides and bromides (63, 85, 86). Zincke (106, 109, 113, 114) established that it was a general property of nitro-substituted benzenesulfenamides to undergo cleavage, with formation of the sulfenyl chloride, when reacted with concentrated hydrochloric acid, either alone or in conjunction with glacial acetic acid. However, the cleavage of sulfenamides by halogen acids does not always lead to the formation of the sulfenyl chloride. If the particular sulfenyl halide is unstable, the disulfide may be obtained instead. Thus, cleavage of benzenesulfenodiethylamide with hydrogen chloride led to the formation of benzenesulfenyl chloride (equation 25), but the action of hydrogen bromide in carbon tetrachloride solution gave phenyl disulfide (64). In contrast to the formation of sulfenyl chlorides from the sulfenamides by heating with concentrated hydrochloric acid, it was found that the action of hot dilute acids resulted in the formation of sulfenimides. Thus, Zincke found that by heating sulfenamides such as XXVII and XXVIII with dilute hydrochloric or acetic acid, ammonia or methylamine was eliminated and the sulfenimides XXVII-A and XXVIII-A were obtained.



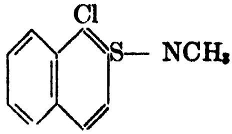
XXVII



XXVII-A

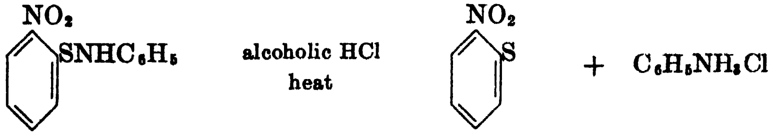


XXVIII



XXVIII-A

Moore and Johnson reported that gentle refluxing of sulfenanilides for extended periods with alcoholic or aqueous solutions of hydrogen chloride resulted in the formation of disulfides and amine hydrochlorides (74, 76).



(53)

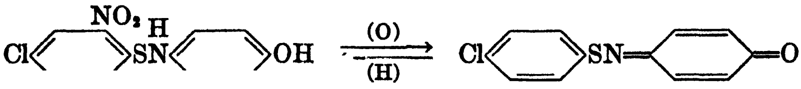
Zincke and Eismayer (108) likewise reported that the action of concentrated hydrochloric acid on 2-chloro-1-naphthalenesulfenanilides led to the formation of disulfides and "disulfoxides", but the sulfenyl chloride could not be isolated.

The sulfenamides are more resistant to hydrolytic scission in cold alkaline media than they are in acid solutions. The action of hot alcoholic solutions of sodium hydroxide, however, effects rearrangements of the sulfenanilides to mercapto diarylamines (see page 323). In attempting to reduce nitro-substituted sulfenanilides, such as 4-chloro-2-nitrobenzenesulfen-*p*-hydroxyanilide, to amino derivatives, Gebauer-Fülnegg and Beatty (38) found that this could not be achieved because cleavage of the sulfenamide linkage occurred even under the mildest conditions which were effective for the reduction of the nitro group, for example, by the use of aluminum amalgam in neutral or aqueous solution.

Because of their resemblances to amines, Zincke attempted to diazotize compounds such as 2-nitrobenzenesulfenamide (109). However, the action of nitrite plus acid resulted in hydrolysis of the sulfenamide. The products obtained were the disulfide and the "disulfoxide," but no indications of products which would be analogous to diazonium chlorides were found. Lecher (64) similarly reported that *p*-toluenesulfenanilide was cleaved by nitrous acid in acetic acid solution. The products reported in this instance were *p*-toluenediazonium acetate and "*p*-tolyl disulfoxide."

5. Oxidations

Although the examples are restricted in number, it seems that oxidation of sulfenamides to the corresponding sulfonamides can readily be effected by alkaline solutions of permanganate or of hydrogen peroxide. This procedure has served as an alternative method for the synthesis of certain sulfonamide derivatives (6, 7, 8). The oxidation of sulfenamides in acid media does not proceed in the same manner. Apparently, hydrolytic scissions accompany the oxidative process, and there results a mixture of more complicated products. Zincke and Farr (109) reported that the action of nitric acid (d = 1.5) on 2-nitrobenzenesulfenamide resulted in a very vigorous reaction, accompanied by deflagration of the sulfenamide. Gebauer-Fülnegg and coworkers (40, 41, 42) made a study of the oxidation of certain sulfenanilides with oxidizing agents such as nitric acid, and potassium dichromate or hydrogen peroxide in conjunction with glacial acetic acid. In none of the experiments were sulfonamides unequivocally identified in the reaction mixtures. The products were generally complex, and in several instances could not be identified. These workers, however, had found that nitrobenzenesulfenyl chlorides reacted with *o*- or *p*-aminophenol to give the corresponding hydroxyanilides (for example, XXIX), and that the latter could be oxidized to the corresponding quinoneimine derivative (XXX) by hydrogen peroxide or potassium dichromate in glacial acetic acid solution (38, 39, 40). By gentle reduction, compound XXX could be reconverted to XXIX.

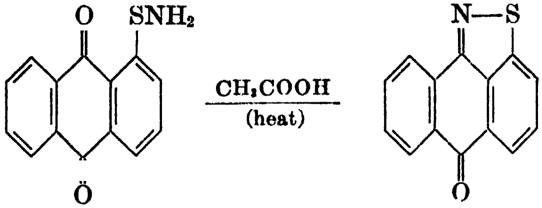


XXIX XXX (54)

Compounds such as XXIX were denoted as "quinonesulfurimines," and their properties and proofs of their structures were reported in the papers already cited. Although these derivatives of benzoquinoneimine could be obtained by the method described above, they were not obtainable by direct reaction of the sulfenyl chloride and quinoneimine. In attempts to obtain an oxime or hydrazone from compound XXX, hydrolysis of the sulfur-to-nitrogen bond occurred and prevented the preparation of such derivatives. The main product of the hydrolytic scissions in these instances was 4-chloro-2-nitrophenyl disulfide (39). In an effort to obtain substances which would be of interest as dyes, Gebauer-Fülnegg and Beatty attempted to introduce auxochrome groups into the "quinonesulfurimines" by reducing the nitro group to the amine. This also could not be achieved because scission of the S—N linkage occurred during the reduction. It was found, however, that the "quinonesulfurimines" formed chelate compounds with chromium, and the possibility of using them as dyes was investigated. While the required chemical processes for mordanting with chromium salts could be achieved, the colors produced were uninteresting and the investigation was not extended (38).

6. *Reactions with carbonyl compounds*

Zincke and coworkers (106, 109, 113, 114) demonstrated that it was a general property of sulfenamides, such as 2-nitrobenzenesulfenamide, 4-chloro-2-nitrobenzenesulfenamide, and 1-chloro-2-naphthalenesulfenamide, to react with acetone and benzaldehyde in a manner which resembles the formation of Schiff bases from primary amines (see, for example, equation 51). These reactions were carried out by heating the sulfenamides with excess acetone in a sealed tube at 100°C. for a few hours, or by boiling with alcoholic solutions of benzaldehyde. The reactions with benzaldehyde took place more readily than with acetone. The products obtained (for example, XXV) were excellently crystalline substances which may find use as derivatives for the sulfenamides. Similar reactions with other ketones and with aldehydes other than benzaldehyde, or with other types of sulfenamides, were not investigated by Zincke, although Vörlander and Mittag (100) reported such reactions for triphenylmethanesulfenamide. An interesting example was also described by Fries and Schürmann (32). These workers obtained the isothiazole analog (XXXI) by heating 1-anthraquinonesulfenamide in glacial acetic acid solution.



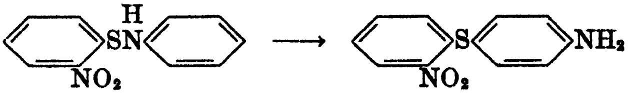
XXXI (55)

7. *Rearrangements of sulfenanilides*

In studies of the reaction between aromatic amines and sulfur, Moore and Johnson (73) corroborated the reports of earlier workers that amino sulfides were formed as products in this reaction, and noted that only those amines which had at least one labile hydrogen atom attached to nitrogen could react with sulfur to yield such products. They therefore postulated that the formation of the amino sulfides was a two-step process as indicated in equation 56.

$$C_6H_5NH_2 \xrightarrow[135\text{–}145°C.]{(S)} \underset{\text{XXXII}}{C_6H_5NHSNHC_6H_5} \rightarrow \underset{\text{XXXIII}}{H_2NC_6H_4SC_6H_4NH_2} \quad (56)$$

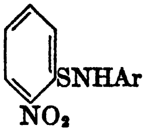
The isolation of an intermediate product corresponding to XXXII could not be achieved because, at the temperature of the aniline–sulfur reaction, even if the intermediate was actually formed, it was completely decomposed. Because the structures of sulfenanilides, ArSNHAr, are analogous to that of the proposed intermediate, Moore and Johnson undertook studies of the rearrangements of these substances. The results of these investigations were subsequently reported in a series of papers. It was found (74, 76) that sulfenanilides such as XXXIV yielded small amounts of amino sulfides, such as XXXV, when simply heated at 150–160°C. for about 5 hr.



(57)

XXXIV XXXV

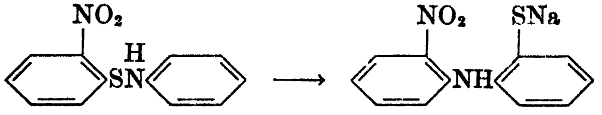
Because rearrangements from nitrogen to carbon are generally favored by the presence of acid, such conditions were studied. Mineral acids could not be used, however, for in their presence hydrolysis of the sulfenamide linkage invariably occurred in preference to rearrangement. Thus, with dilute hydrochloric acid, disulfides were isolated as the products of hydrolytic scission, but products of rearrangement could not be detected (74, 76). Disulfides were also formed when sulfenanilides were heated in the presence of amine hydrochlorides, and also on long digestion with glacial acetic acid. If the sulfenanilides were heated in the presence of excess aromatic amine, however, the amino sulfides were obtained in satisfactory yields. Thus, when 2-nitrobenzenesulfenanilide (XXXIV) was heated for 6 hr. at 180–190°C., with excess of aniline present, *p*-(2-nitrophenylthio)aniline (XXXV) was obtained in 70 per cent yield. In such experiments, in every case but one, the rearrangement reaction gave only a single product. In the one variant instance, when 2-nitrobenzenesulfen-*o*-toluidide was heated with excess *o*-toluidine, two isomeric amino sulfides were obtained. This result was interpreted to indicate that ortho as well as para rearrangement may occur, and to imply that the rearrangement of sulfenanilides occurred in two steps: formation of the ortho isomer, followed by rearrangement of this to the more stable *p*-amino sulfide. It was later determined that if the para-position of the sulfenanilide was blocked, rearrangement to the ortho-position occurred. Whenever possible, however, rearrangement to the para-position predominated. It was also found that in the course of the reaction the anilide group in one sulfenanilide could be displaced by another, and that in this way, there could be formed an amino sulfide corresponding to the externally added amine (76). Thus, when 2-nitrobenzenesulfenanilide was heated at 180–190°C. with an excess of *o*-toluidine, *p*-(2-nitrophenylthio)-*o*-toluidide was obtained. It was established that aniline, *o*-toluidine, and *p*-toluidine were able to displace one another in the rearrangements of the respective sulfenamides to the amino sulfides. *o*-Chloroaniline, however, did not displace the anilide groups in structures corresponding to XXXVI (Ar = phenyl, *o*- or *p*-tolyl).



XXXVI

For example, when 2-nitrobenzenesulfenanilide (Ar = C_6H_5) was heated at 180–190°C. in the presence of excess *o*-chloroaniline, compound XXXV was obtained in 70 per cent yield. Moreover, it was found that *o*-chloroaniline was replaced from its anilides by other aromatic amines, such as aniline or *o*-toluidine, with particular ease. Tabulations of such experiments concerning displacements of one amine by another in the rearrangements of sulfenanilides have been prepared by Moore and Johnson (76). A similar discussion of such rearrangements is given in a patent (56).

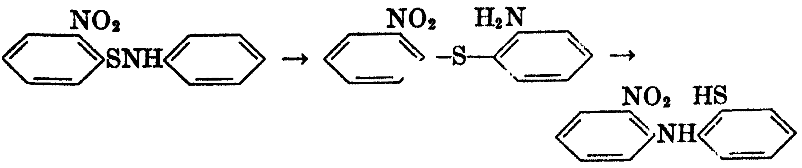
When certain nitro-substituted benzenesulfenanilides are heated in alcoholic sodium hydroxide solutions, the rearrangement takes a different course from the one just described above. Instead of amino sulfides, the products obtained were the corresponding *o*-mercapto diaryl amines (75). For example, if 2-nitrobenzenesulfenanilide was refluxed with dilute alcoholic sodium hydroxide solution for 3 hr., an 87 per cent yield of product XXXVII was obtained.



XXXVII

(58)

The isolation product XXXVII, whose structure was established by conversion to the known thiomethyl ether as described by Wight and Smiles (102), definitely established that 2-nitrobenzenesulfenanilides were capable of undergoing ortho as well as para rearrangements (75). That is, direct heating resulted in the formation of *p*-amino sulfides, while treatment with alcoholic sodium hydroxide favored ortho rearrangement to mercapto diarylamines. In the latter type of rearrangement, it is interesting to note that while 2-nitrobenzenesulfenanilide rearranged very easily to product XXXVII, 4-nitrobenzenesulfenanilides did not rearrange under the same conditions. 2-Nitro-4-chlorobenzenesulfenanilides did, however, rearrange. These differences were considered to indicate that the substitution of the nitrogroup in the para-position did not activate the carbon atom attached to the amino nitrogen to the same extent as was done by a nitro group in the ortho-position. A tabulation of these rearrangements may be found in reference 77. The possibility that the rearrangement of 2-nitrobenzenesulfenanilides to diarylamines occurs through the intermediate formation of the ortho amino sulfides was suggested by Moore and Johnson (75), but they considered that the evidence available for its support was not adequate (equation 59).



(59)

VI. Alkyl and Aryl Sulfenates

Substances corresponding to the formula RSOR′, in which R′ may be an alkyl or aryl radical, may be considered as esters of the sulfenic acids. In accord with this viewpoint, they have also been designated as sulfenates. These compounds are isomeric with the sulfoxide, but it has been clearly established that the two classes of substances are distinctly different.

A. PREPARATION

The only instances of the direct esterification of a sulfenic acid are the preparations of methyl and ethyl 1-anthraquinonesulfenates (table 4). The most general procedure, however, consists in the reaction of sodium alkoxides or phenoxides with sulfenyl halides (60, 64, 84, 106, 108, 109, 113, 114).

$$\mathrm{RSCl} + \mathrm{NaOR'} \rightarrow \mathrm{RSOR'} + \mathrm{NaCl} \qquad (60)$$

Presumably, sulfenyl thiocyanates may also be used in place of the sulfenyl halides. Connor (21) calls attention to the fact that the reaction of alkyl hypochlorites with mercaptides does not give sulfenic esters, but that disulfides are formed instead.

$$2\mathrm{RSNa} + \mathrm{R'OCl} \rightarrow \mathrm{RSSR} + \mathrm{R'ONa} + \mathrm{NaCl} \qquad (61)$$

As already mentioned (page 272), 1-anthraquinonesulfenyl bromide reacted with boiling methanol to give the corresponding methyl sulfenate (30).

B. TABULATION

Table 4 lists those alkyl and aryl sulfenates which were encountered in the course of this literature survey.

TABLE 4

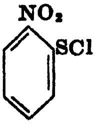
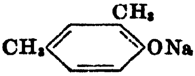
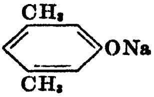
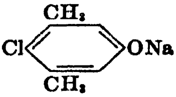
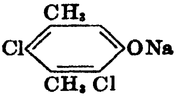
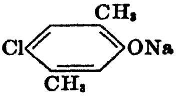
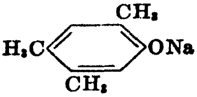
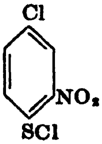
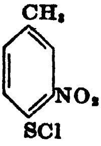
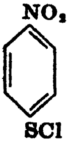
Alkyl and aryl sulfenates

Ethyl 1-anthraquinonesulfenate, $C_{16}H_{12}O_3S$	Red needles. M.p. 149°C. Prepared from the sulfenyl chloride or bromide by reaction with ethyl alcohol, or from the sulfenic acid and ethyl sulfate (30, 32).
Ethyl trimethylmethanesulfenate, $C_6H_{14}OS$	Colorless liquid. B.p. 64°C./89 mm. From the sulfenyl iodide and sodium ethoxide in ether solution (84). The methyl ester was prepared in similar manner (87).
Methyl 1-anthraquinonesulfenate, $C_{15}H_{10}O_3S$	Orange-red needles. M.p. 189°C. From the sulfenyl bromide or the sulfenic acid by boiling with methanol (30).
Methyl benzenesulfenate, C_7H_8OS	Colorless liquid. B.p. 88–89°C./4 mm. (corr.). From benzenesulfenyl chloride and sodium methoxide, in methanol, at 0°C. Yield, 36 per cent. Considerable phenyl disulfide formed simultaneously. Odor resembles that of thiophenol (64).
Methyl 1-chloronaphthalene-2-sulfenate, $C_{11}H_9OSCl$	Nearly colorless oil. From the sulfenyl chloride and sodium ethoxide, in hexane, by shaking at room temperature (108).

TABLE 4—*Concluded*

Nitrobenzenesulfenates

All of the examples listed below were prepared from the corresponding sulfenyl chlorides and sodium alkoxides or phenoxides

SULFENYL CHLORIDE	ALKOXIDE OR PHENOXIDE	MELTING POINT	REFERENCE
		°C.	
	CH_3ONa	54	(109)
	C_2H_5ONa	26	(109)
	C_6H_5ONa	72	(109)
		85	(60)
		74	(60)
		118–120	(60)
		125–127	(60)
		120	(60)
		103	(60)
	CH_3ONa	111–112	(106)
	C_2H_5ONa	73–74	(106)
	C_6H_5ONa	75	(106)
	CH_3ONa		(114)
	CH_3ONa	49	(113)

C. PROPERTIES

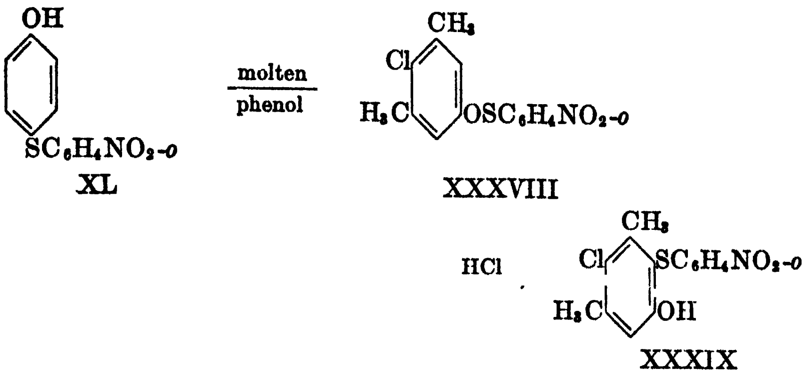
The majority of the reported sulfenic acid esters are solids of definite melting points. The thermal stabilities of these compounds are reflected in the reports that methyl trimethylmethanesulfenate and methyl benzenesulfenate were isolated by distillation at relatively high pressures (see table 4), as well as by the fact that the aryl 2-nitrobenzenesulfenates did not decompose until heated to 120°C. (60). The 2-nitrobenzenesulfenates were invariably reported to be yellow, but since some of the other members were found to be colorless, color is apparently not associated with the sulfenate linkage. In general, the sulfenates were found to be insoluble in water, sparingly soluble in alcohol, and more soluble in ether, benzene, etc.

It might be expected that the oxidation of sulfenates would lead progressively to esters of sulfinic acids and then to sulfonates. This simple addition of oxygen does not seem to occur. Zincke found that the oxidation of alkyl 2-nitrobenzenesulfenates with hydrogen peroxide led to the formation of the free sulfinic acids rather than the esters. At the same time, the formation of smaller proportions of "disulfoxides" was observed. In the oxidation of aryl 2-nitrobenzenesulfenates, the corresponding sulfonic acid ester could also not be obtained. The action of hydrogen peroxide or other oxidizing agents, in warm glacial acetic acid, resulted in disruption of the sulfenates (60).

The hydrolytic stabilities of alkyl sulfenates appear to be somewhat greater than those of the corresponding aryl derivatives. Zincke (109) found that if the phenyl sulfenates were not kept in a vacuum desiccator, rapid decomposition, with the formation of phenol, occurred. Methyl 1-chloro-2-naphthalenesulfenate, however, was also very readily decomposed by exposure to the air (108). In comparing various phenyl 2-nitrobenzenesulfenates, Learmonth and Smiles (60) remarked that those of the esters which contained more fully substituted phenyl groups were more stable than phenyl 2-nitrobenzenesulfenate itself. In passing, it may be noted that methyl *p*-nitrobenzenesulfenate was reported to be less stable than the corresponding *o*-nitrobenzenesulfenate. This is reminiscent of the similar relation between *p*-nitrobenzenesulfenyl chloride and *o*-nitrobenzenesulfenyl chloride.

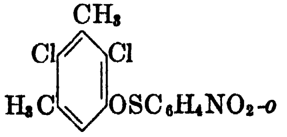
Concentrated hydrochloric acid converts certain sulfenic acid esters to the corresponding sulfenyl chlorides (106, 108, 109, 113, 114). On the other hand, alkaline or neutral hydrolysis leads to the formation of disulfides and "disulfoxides" (108). Zincke observed that the reactions of the sulfenates with sodium hydroxide resulted in the formation of characteristic colors which he ascribed to the intermediate existence of the salts of sulfenic acids. Learmonth and Smiles (60) reported that warm alkali effected the hydrolysis of aryl 2-nitrobenzenesulfenates, but they did not indicate the products obtained.

Corresponding to the rearrangements of the sulfenanilides, as demonstrated by Moore and Johnson, the work of Learmonth and Smiles has shown that phenyl 2-nitrobenzenesulfenates are converted, under the influence of hydrogen chloride in benzene solution, into hydroxy sulfides. The conversion of the sulfenate XXXVIII into the hydroxy sulfide XXXIX is a suitable example.



(62)

It should be noted, however, that in the rearrangements of sulfenanilides acid conditions could not be used, while in the rearrangements of the aryl sulfenates such conditions are required (see page 322). The yields of hydroxy sulfides obtained in such rearrangements permit this reaction to serve as a convenient means for their preparation. It was also found (60) that an external phenol could displace the original aryl group present in the sulfenate. For example, in the presence of molten phenol, the sulfenate XXXVIII yielded the sulfide XL (equation 62). This ability for one phenol to displace another in the course of the rearrangement reaction, together with other evidence concerning the orientation of the sulfides produced, led Learmonth and Smiles to consider that the conversion of the aryl sulfenates to hydroxy sulfides was not a true intramolecular rearrangement. It was also noted that rearrangement does not always occur. Thus, in the attempt to rearrange 3,5-dimethyl-2,4-dichlorophenyl 2-nitrobenzenesulfenate (XLI) by the standard procedure which was effective in other



XLI

instances, there was obtained the chlorophenol and 2-nitrobenzenesulfenyl chloride; but the hydroxy sulfide, to be expected if rearrangement occurred, was not to be found among the reaction products (60). The possibility that such cleavage of the sulfenic ester may also occur in cases where rearrangement is observed, and that the hydroxy sulfide then results from a secondary reaction between the sulfenyl chloride and the phenol, deserves consideration.

VII. SULFENIC ANHYDRIDES

The sulfenic anhydrides (RSOSR) are formed mainly as the products of hydrolysis of sulfenyl chlorides (106, 108, 109, 113, 114). Presumably they arise in the following fashion:

$$\text{ArSCl} \xrightarrow{\text{HOH}} \text{ArSOH} \xrightarrow{\text{ArSCl}} \text{ArSOSAr} \qquad (63)$$

While each of the nitro-substituted benzenesulfenyl chlorides investigated by Zincke was reconverted to a corresponding sulfenic anhydride, the experiences with these were so nearly alike, and compare so closely to instances cited by other authors, that the description of the experiments with 2-nitrobenzenesulfenic anhydride (109) will serve for illustrative purposes. When 2-nitrobenzenesulfenyl chloride was shaken for about 5 hr. with twenty times its weight of water, at room temperature, a smooth hydrolysis ensued to form 2-nitrobenzenesulfenic anhydride. This substance, like the other members of its class, was difficultly soluble in petroleum ether, ether, and alcohol, but more readily soluble in benzene, glacial acetic acid, chloroform, or acetone. With concentrated hydrochloric acid, the anhydride was converted to 2-nitrobenzenesulfenyl chloride in nearly quantitative yield. The conversion to the sulfenyl chloride could also be readily effected by use of phosphorus pentachloride in ether solution. Accompanying the reaction of the anhydride with aqueous ammonia or sodium hydroxide, there was the development of the characteristic color of the salts of sulfenic acids. This color disappeared on heating, on addition of acid, or if the solution was allowed to stand for some time at room temperature. In alcohol, ammoniacal solutions retained their color for considerably longer periods than aqueous solutions. If a freshly prepared ammoniacal solution was treated with lead acetate, there was precipitated a blue product, presumably the lead salt, which rapidly became colorless. Zincke suggested that such reactions implied an amphoteric character for sulfenic acids. That is, the reaction of the anhydrides with hydrochloric acid indicated their basic character, and their reaction with lead acetate or bases, to give the transitory metal sulfenates, showed an acidic character.

$$\begin{tikzcd}
 & & \mathrm{RSCl} \\
\mathrm{RSOSR} \arrow[r, "\mathrm{HOH}"] & \mathrm{RSOH} \arrow[ur, "\mathrm{HCl}"] \arrow[dr, "\mathrm{Pb^{++}}"'] & \\
 & & \mathrm{(RSO)_2Pb}
\end{tikzcd} \tag{64}$$

The products isolated from the alkaline hydrolysis of 2-nitrobenzenesulfenic anhydride were chiefly 2-nitrophenyl disulfide and 2-nitrobenzenesulfinic acid. The "disulfoxide" was considered to be an intermediate product in the formation of the disulfide and sulfinic acid, but it was not actually isolated in this instance. In other cases (113) the "disulfoxide" was reported among the products of hydrolysis. It was found that the decomposition of 2-nitrobenzenesulfenic anhydride into the disulfide and sulfinic acid occurred spontaneously when the anhydride was covered with a layer of aqueous sodium hydroxide. This immediate formation of the insoluble disulfide explained why the sulfenic anhydrides never seemed to dissolve completely in sodium hydroxide solutions. (Notations regarding 1-chloro-2-naphthalenesulfenic anhydride are recorded in reference 108, and the anhydrides of the anthraquinonesulfenic acids have already been referred to in Section II.) The various nitro-substituted benzenesulfenic anhydrides which were prepared by Zincke were definite products which gave correct analyses for the elements, but they did not display sharp melting temperatures. Examples of the sulfenic anhydrides which were encountered in this literature survey are listed in table 5.

TABLE 5

Sulfenic anhydrides

1-Anthraquinonesulfenic anhydride, $C_{28}H_{14}O_5S_2$	From 1-anthraquinonesulfenic acid by heating. Not obtained pure (30).
2-Anthraquinonesulfenic anhydride, $C_{28}H_{14}O_5S_2$	Colorless crystals. M.p. 260°C. (decomposition). From 2-anthraquinonesulfenyl chloride by hydrolysis (32).
1-Chloro-2-naphthalenesulfenic anhydride, $C_{20}H_{12}OS_2Cl_2$	Pale yellow crystals from toluene. M.p. 140°C. (decomposition). From the sulfenyl chloride by alkaline hydrolysis (108).
4-Chloro-2-nitrobenzenesulfenic anhydride, $C_{12}H_6O_5N_2S_2Cl_2$	Yellow plates. Sinter at 115–116°C. but do not melt unless heated above 200°C. May be recrystallized from glacial acetic acid (106).
2-Nitrobenzenesulfenic anhydride, $C_{12}H_8O_5N_2S_2$	Yellow plates from benzene. Darken at 92–93°C., fuse, and do not remelt until heated above 180°C. By hydrolysis of the chloride with water at room temperature. Some disulfide formed as side product (109).
4-Nitrobenzenesulfenic anhydride, $C_{12}H_8O_5N_2S_2$	Yellow leaves. Darken at 126°C. and melt with decomposition at 160°C By hydrolysis of the chloride with dilute alcohol or acetic acid (113).
2-Nitro-4-methylbenzenesulfenic anhydride, $C_{14}H_{12}O_5N_2S_2$	Pale yellow crystalline powder. M.p. 194°C. with previous discoloration. By hydrolysis of the sulfenyl chloride with water (114).

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THE DISSOCIATION OF STRONG ELECTROLYTES

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The difficulties of the classical theory of electrolytes with respect to strong electrolytes and various attempts at reconciling the theory with the experimental data are briefly reviewed. The theory of Debye and Hückel furnishes methods of separating the effects of interionic attraction and incomplete dissociation in dilute solutions of moderately strong electrolytes. The intrinsic limit of these methods is discussed. A clear distinction is made between molecules and interacting ions. A reliable, though not yet precise, method of determining the degree of dissociation of strong electrolytes is based on the intensity of Raman lines. The effect of incomplete dissociation on other properties like apparent molal volume, molal refractivity, extinction coefficient, heat of dilution, and heat capacity is ascertained. The molecular constitutions of nitric and perchloric acids are described. A few results are available for other substances.

I. INTRODUCTION

The problem of the dissociation of strong electrolytes is as old as the theory of Arrhenius (4). An address given by Arrhenius (5) in Chicago in 1912 presents a good deal of information on the birth of his theory. It is perhaps a little surprising to read that as early as in 1888 Planck, as well as van't Hoff, aired just one objection against the revolutionary theory: namely, that the dissociation constant was not constant (5, pages 361, 362).

At no time did there exist any real accord between the classical theory of electrolytes and the available experimental data on strong electrolytes. The success of Arrhenius' theory, however, was so overwhelming that its failure in *one* respect could be neglected at first. But the classical theory was still widely applied to strong electrolytes even when its failure in this field was generally recognized. This strange and unsatisfactory situation was due mainly to two causes: the lack of a better theory, and reluctance to adopt correct thermodynamic methods of handling imperfect solutions. The development of a consistent theory culminated in the theory of Debye and Hückel in 1923, at the same time that Lewis and Randall in their textbook presented their thermodynamic methods in a final form which soon was generally accepted.

Before 1923 the problem of strong electrolytes was frequently expressed in the following alternative: incomplete dissociation according to Arrhenius, or complete dissociation and an appreciable influence of interionic electrostatic forces. The simplification implied in this alternative was not unjustified. In a case like this it is, at first, an entirely sound attempt to explain the facts by means of one of two effects rather than by a superposition of both.

Today the numerous discussions of the classical problem are mainly of historical interest. A long and hard struggle between a well-established theory and discordant experimental facts always presents a fascinating and instructive picture. The retrospective observer notes the efforts to save the old theory, repeated again and again in ever new ways. He admires a number of clear and critical discussions of the data and inevitable conclusions. He enjoys the bold attempts to start from scratch with a new theory, attempts which at first are based on arbitrary and erroneous assumptions as well as on insufficient experimental data, and which gradually improve until success is achieved.

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In the following three sections an attempt is made to outline this development, which came to a conclusion in 1923.

The problem of the dissociation of strong electrolytes was entirely changed by the theory of Debye and Hückel. The question could no longer be an alternative between incomplete dissociation and ionic interaction. The electrostatic effect was quantitatively established in the limit of low concentrations. Attempts at extending the theory to higher concentrations were partially successful but soon reached a barrier of insuperable difficulties. One of the principal problems still open was the delineation of the influences of electrostatic interaction and incomplete dissociation.

The later sections of this article review the development of this problem.

II. ATTEMPTS TO SAVE THE CLASSICAL THEORY

It will be convenient to list, for the special case of a binary electrolyte, the relationships which express the classical theory of electrolytes:

$$\bar{F}_i = F_i^0 + 2RT \ln (\alpha c) \tag{1}$$

$$\vartheta = 3.716(1 + \alpha)c \tag{2}$$

$$K_c = \alpha^2 c/(1 - \alpha) \tag{3}$$

$$\alpha = \Lambda/\Lambda_0 \tag{4}$$

($\bar{F}_i$ = partial molal free energy of the ions; α = degree of dissociation; c = concentration; ϑ = freezing-point depression of an aqueous solution; Λ = molal conductivity; Λ_0 = limit of Λ for $c = 0$.) Each of the first three relations expresses the assumption that the electrolyte forms an ideal solution. Only the relation of Arrhenius (equation 4), together with the data of Kohlrausch, could be expected to furnish values of high precision before the modern technique of determining electromotive forces (G. N. Lewis, A. A. Noyes) and freezing points (L. H. Adams, G. Scatchard) was inaugurated.

The experimental material of the earlier period has been reviewed and very clearly discussed by A. A. Noyes (101) and Noyes and Falk (103). While it is usually a difficult task to draw safe conclusions from complex data of low accuracy, two facts were early recognized: *(1)* the deviations between the degrees of dissociation, determined by different methods, are significant at unexpectedly low concentrations, and *(2)* the "dissociation constant" K_c (equation 3) is not a constant but changes rapidly with the concentration.

Very early, numerous suggestions were made to replace the mass-action law (equation 3) by some empirical formula (*cf.* 7, 134, 141, 145). Considering the thermodynamic connection of the first three equations, these formulas were apt to destroy the classical theory rather than save it, without furnishing any theoretically significant substitute.

No attempt to arrive at a more general theory could appear to be more logical and promising than that of Jahn (71) and Nernst (99). They abandoned the assumption of a perfect solution and developed the deviation of the partial molal free energy from equation 1 into a Taylor series with respect to c. Actually, this idea was not quite new. It had been suggested and applied to non-electrolytes with obvious success by Margules a few years before. What was the reason that a method as general as a development into a Taylor series could fail just for electrolytes? Today the reason can be easily understood. The Taylor development is restricted only by a single, very mild condition: A series extended to the n^{th} order requires the existence and finiteness of the first $n + 1$ derivatives in the whole range. But this condition is not satisfied by electrolyte solutions. Since Debye and Hückel demonstrated that the non-ideal part of the partial molal free energy of an electrolyte contains a $c^{\frac{1}{2}}$-term, no differential quotient with respect to c exists for $c = 0$. For this reason the development into a power series with respect to c could not be successful.

Many attempts were made to save the classical theory by assumptions regarding secondary disturbing effects like hydration and the formation of complex ions. These effects are undoubtedly important in certain cases. The idea that they are *generally* responsible for all deviations from the perfect solution, going back essentially to a suggestion of Dolezalek (34), has led to entirely arbitrary and unjustified conclusions. Attempts were also made to change equation 4 by introducing an arbitrary function of the viscosity of the solution (147).

Step by step the defense of the old theory had yielded ground. After about twenty-five years the conclusion was inevitable that the mass-action law, recognized as thermodynamically linked to the theory, was inconsistent with the experimental data. The last line of defense was the assumption that the mass-action law held only at very high dilution. This idea was proposed in two different ways.

Kraus and Bray (14, 78) succeeded in representing extensive data on non-aqueous and aqueous solutions by means of the equation:

$$B = K_c - Ac_i^h \tag{5}$$

In this empirical relation, K_c is defined by equation 3, c_i is the concentration of the ions, and A, B, and h are individual constants. The same function was proposed independently by MacDougall (88). A similar formula was suggested by Bates (*cf.* 148).

The exponent h was found to depend mainly on the solvent and to decrease with increasing dielectric constant. For aqueous solutions Kraus and Bray obtained values close to $h = 0.6$. Rosenstein (132) represented his colorimetric determinations of the dissociation constant of phenolphthalein in the presence of neutral salts by equation 5 with $h = \frac{1}{2}$. His formula, indeed, approximates the limiting law of Debye and Hückel at low ionic concentrations.

If the equation of Kraus and Bray holds with $h < 1$, differentiation of equation 5 furnishes the result:

$$\lim_{c \to 0} \frac{\mathrm{d}K_c}{\mathrm{d}c} = \infty \tag{6}$$

The classical law, therefore, can be said to hold only in a very restricted sense. Actually, Kraus and Bray found that the deviations expressed by the term Ac_i^h were appreciable down to concentrations below $c = 0.001$.

Washburn (148), too, assumed the validity of the classical theory as a limiting law and of equation 4, but he included in his assumption the relation

$$\lim_{c \to 0} \frac{\mathrm{d}K_c}{\mathrm{d}c} = 0 \tag{7}$$

This condition was used for the determination of Λ_0. The modern technique of the measurement of conductivity started from the work of Washburn and Weiland (148, 150), who obtained precise data for concentrations down to $c = 0.00002$.

But the result was not a very convincing confirmation of the assumption (58, 77a, 148). While the extrapolated value for potassium chloride at 25°C. was $K_c = 0.020 \pm 0.001$, the value $K_c = 0.0524$ was obtained for as low a concentration as $c = 0.001$. Again, the validity of the classical law appeared to be restricted to extreme dilution. It also may have been hard to understand that the dissociation constant of potassium chloride appeared to be about ten times smaller than that of an obviously weaker electrolyte like iodic acid (*cf.* table 1).

A footnote in Washburn's paper (page 151) furnishes the best explanation for all attempts to save the classical law: "The theoretical basis of the mass action law for a sufficiently dilute solution being almost purely thermodynamic in character, . . . ". This reasoning would have been perfectly correct, just as the method of Jahn and of Nernst, if the non-perfect part of the partial free energy of an electrolyte could be developed into a Taylor series with respect to the concentration.

III. CRITICAL DISCUSSIONS

van Laar appears to have been the first to call attention to the influence of electrostatic interaction on the thermodynamic properties (143).

A. A. Noyes, summarizing the results of a series of important experimental investigations (102), concluded that the ionization of strong electrolytes is essentially different from chemical processes, including the dissociation of weak electrolytes. His main reasons are: The degree of ionization of strong electrolytes depends on the valence type rather than on the chemical character, temperature is of little influence, the mass-action law is not satisfied, and the molar extinction coefficients are independent of the concentration.

Analyzing the various possible reasons of the anomalies of strong electrolytes, Wegscheider (149) pointed out that a test of the mass-action law in combination with equation 4 is fair only if Λ_0 is chosen so that a minimum variation of K_c is obtained. One cannot test equation 3 if Λ_0 is determined by an extrapolation inconsistent with equation 3. Washburn, in the work reported before, made use of this conclusion.

If the anomalies are due to electrostatic interaction and therefore depend on the valence type rather than on the chemical nature of the electrolyte, there should be a certain *ionic* concentration below which the classical laws should hold for uni-univalent electrolytes, weak or strong. This strict condition was stated by Wegscheider. He found from the data available for weak electrolytes that the limit is about $c = 0.03$. Washburn's later result that potassium chloride exhibits large deviations even at much lower concentrations might have been interpreted as final evidence of the failure of the classical theory.

The retrospective observer, of course, can easily put his finger on omissions and inconsistencies. But already in 1909 Lewis' paper, "The Use and Abuse of the Ionic Theory" (80), discussed the principal inconsistencies of the classical theory as it was applied to strong electrolytes. A few years later, Lewis developed correct and simple methods for treating the thermodynamic properties of electrolyte solutions (81). At the same time, he pointed out that the dependence of the transference number on the concentration immediately invalidated equation 4.

IV. ELECTROSTATIC INTERACTION AND COMPLETE DISSOCIATION

Malmström (94) proposed, in 1905, the first quantitative theory of the influence of electrostatic interaction between the ions on the free energy. While his paper was completely forgotten, similar ideas aroused considerable interest when proposed by Ghosh (54) thirteen years later.

Malmström's work was inconclusive because he still used equation 4 and because he did not assume complete dissociation of strong electrolytes. This bold step was undertaken a little later by Bjerrum (10) and Sutherland (142). Bjerrum drew the logical conclusion from the constancy of the extinction coefficients, previously pointed out by Noyes.

The application of the later theories of electrostatic interaction of Milner (95) and Hertz (68) and the first discussions of the theory of Debye and Hückel were based on the auxiliary assumption of complete dissociation.

V. MODERATELY STRONG ELECTROLYTES

The success of the theory of Debye and Hückel was correctly interpreted as proving the complete dissociation of strong electrolytes in dilute solution. As this conclusion was based on experimental facts and an approximately valid theory, it could never have axiomatic significance. "Complete dissociation" merely meant that electrostatic interaction, which according to the conclusive deductions of Debye and Hückel must be taken into account in any case, is sufficient to represent the data without an assumption of the existence of undissociated molecules.

In principle, of course, one has always to consider the influence of both interionic forces and incomplete dissociation. For the reasons advanced by Wegscheider, the interionic forces can be neglected or taken care of by minor corrections in the case of solutions of weak electrolytes, while the formation of molecules may be neglected for dilute solutions of strong electrolytes. This leaves an intermediate field, the moderately strong electrolytes, in which both effects are considerable even in dilute solutions.

The methods for the calculation of the degrees of dissociation and the dissociation constant of a moderately strong electrolyte have been developed by Gross and Halpern (57), Sherrill and Noyes (138), and MacInnes (90). For a binary electrolyte, equations 3 and 4 are to be replaced by

$$K = \frac{(\alpha\beta_i)^2 c}{(1 - \alpha)\beta_u} = \frac{\gamma^2 c}{(1 - \alpha)\beta_u} \tag{8}$$

$$\alpha = \Lambda/\Lambda_e \tag{9}$$

where K denotes the thermodynamic dissociation constant, β_i and β_u the activity coefficients of the ions and the molecules, and $\gamma = \alpha\beta_i$ the stoichiometric activity coefficient. For low concentrations, β_i is determined by the limiting law of Debye and Hückel

$$\log \beta_i = -0.505(\alpha c)^{1/2} \tag{10}$$

(aqueous solutions of a uni-univalent electrolyte at 25° C.), while $\beta_u = 1$. The quantity Λ_e represents the sum of the mobilities of the two ions. It is estimated under the assumption that Kohlrausch's law of independent migration is valid. For instance, it is assumed that for a solution of iodic acid of the concentration c and the ionic concentration αc, the quantity Λ_e is obtained from the molar conductivities of properly chosen strong electrolytes of the concentration αc by

$$\Lambda_e(c;\ \mathrm{HIO_3}) = \Lambda(\alpha c;\ \mathrm{HCl}) + \Lambda(\alpha c;\ \mathrm{NaIO_3}) - \Lambda(\alpha c;\ \mathrm{NaCl}) \tag{11}$$

Instead of using equations 9 and 11, Onsager (109) estimated dissociation constants from the deviations of conductivity data from the limiting law which he had derived. Similar methods were proposed and extensively used by Davies (6, 13, 27, 28, 29, 89, 97, 128, 129).

These methods permit the calculation of α either from Λ or from γ for low ionic concentrations αc. The dissociation constant K is calculated from equation 8. If a variation with the concentration indicates that the assumptions are not completely justified, the best value of K is obtained by extrapolation to $c = 0$. The calculation of α is carried out without difficulty by iterated approximation. Table 1 contains examples of dissociation constants obtained by these methods and by earlier classical calculations. The authors quoted are in many cases responsible only for the calculation, not for the experimental data.

A few determinations by means of extinction coefficients are included for comparison; the method will be discussed later.

The methods for taking into account the interionic forces have greatly increased the accuracy of dissociation constants of weaker electrolytes. For acetic acid, for instance, Harned and Ehlers (67) derived $K = 1.754$ from electro-

TABLE 1

Dissociation constants of some moderately strong electrolytes

SUBSTANCE	K	TEMPERATURE °C.	METHOD	YEAR	REFERENCE
TlCl	0.31	18	Conductivity	1927	Onsager (109)
	0.30	18	Conductivity	1927	Davies (29)
	0.23	25	E.M.F., solubility	1945	Garrett *et al.* (12, 52, 69)
HIO_3	0.262	0	Freezing point	1934	Abel, Redlich, and Hersch (2)
	0.19	18	Conductivity	1934	Abel, Redlich, and Hersch (2)
	0.18	25	Conductivity, freezing point	1903	Rothmund and Drucker (133)
	0.17	25	Conductivity	1927	Onsager (109)
	0.1686	25	Conductivity	1933	Fuoss and Kraus (51)
	0.163	25	Solubility	1939	Naidich and Ricci (98)
	0.167	25	Indicator	1944	Halban and Brüll (59a)
Trichloroacetic acid	0.217	20	Indicator	1944	Halban and Brüll (59a)
	0.232	25	Indicator	1944	Halban and Brüll (59a)
Tribenzylmethylammonium chloride	0.179	18	Conductivity	1912	Drucker (36)
Tribenzylmethylammonium bromide	0.139	18	Conductivity	1912	Drucker (36)
Picric acid	0.164	—	Distribution, freezing point	1903	Rothmund and Drucker (133)
Dichloroacetic acid	0.14	0	Freezing point	1930	Redlich and Rosenfeld (126)
$H_4P_2O_7$	0.14	18	Conductivity, distribution	1909	Abbott and Bray (1)
$PbCl^+$	0.064	25	Solubility	1901	von Ende (146)
	0.0775	25	Extinction	1931	Fromherz and Kun-Hou Lih (49)
	0.1	25	E.M.F.	1938	Güntelberg (59)
$PbBr^+$	0.071	25	Extinction	1931	Fromherz and Kun-Hou Lih (49)

TABLE 1—*Continued*

SUBSTANCE	K	TEMPERATURE	METHOD	YEAR	REFERENCE
		°C.			
PbI^+	0.0345	25	Extinction	1931	Fromherz and Kun-Hou Lih (49)
H_2SO_4 in methanol	0.029	25	Conductivity	1943	Kanning *et al.* (73)
Nitroacetic acid	0.0208	18	Reaction rate	1943	Pedersen (110)
HSO_4^-	0.013		Conductivity	1903	Luther (85)
	0.03	25	Various	1910	Noyes and Stewart (104)
	0.015		Various	1911	Jellinek (72)
	0.013	25	Conductivity	1911	Drucker (35)
	0.017	18	E.M.F.	1920	Drucker (37)
	0.02		Colorimetric	1924	Kolthoff (76)
	0.030	25	E.M.F.	1926	Livingston (83)
	0.0115	25	Conductivity	1926	Sherrill and Noyes (138)
	0.0180	15	E.M.F.	1934	Hamer (62)
	0.0127	25			
	0.0084	40			
	0.0102	25	Conductivity	1940	Singleterry (140)
	0.01797	5	Colorimetric	1940	Young and Singleterry (140, 153b)
	0.01357	15			
	0.01015	25			
	0.00755	35			
	0.00558	45			
	0.00412	55			
H_2SO_3	0.012	25	Conductivity	1926	Sherrill and Noyes (138)
	0.0172	25	Conductivity	1941	Tartar (142a)
H_3PO_4; $H_3P_2O_7^-$	0.011	18	Conductivity, distribution	1909	Abbott and Bray (1)
H_3PO_4	0.0083	18	Conductivity	1926	Sherrill and Noyes (138)
$HSeO_4^-$	0.01	25	E.M.F.	1942	Gelbach and King (53)
o-Nitrobenzoic acid	0.0060	25	Conductivity	1926	MacInnes (90)
	0.006957	18	Conductivity	1933	Fink and Gross (44)
Chloroacetic acid	0.001396	25	Conductivity	1933	Saxton and Langer (135)

motive forces, while MacInnes and Shedlovsky (91, 92) found 1.753 from conductivities (25°C.; *cf.* also 135). The galvanic cells devised by Harned and other authors were especially efficient in eliminating the influence of electrostatic forces. Precise measurements of the dissociation of weak electrolytes have been reviewed by Harned and Owen (67a).

In the group of moderately strong electrolytes the second dissociation of sulfuric acid has been studied most frequently. This case illustrates the progress which has been made in this field. The discrepancies between the results of the earlier authors are due to the uncertainty of the theoretical basis, but the recent results of Young and his coworkers (140, 153b) are reliable within the much narrower limits of experimental error and hardly affected by any uncertainty of interpretation (*cf.* also 67a). Young (153a) also showed that an apparent deviation of the heat of dilution from the theory of Debye and Hückel was due to the incomplete dissociation of the hydrosulfate ion.

But the range covered by conclusions from thermodynamic properties and conductivities has hardly been increased. Iodic acid furnishes a characteristic example. While the recent determinations are more precise and based on a much stronger theory, the classical result of Rothmund and Drucker had furnished a good approximation (*cf.* table 1).

It can be demonstrated, indeed, that the dissociation constant of iodic acid is already close to the upper limit of the range to which the methods discussed in this section can be applied.

These methods are invariably based on the assumption that the influence of the interionic forces can be predicted without recourse to experimental data for the individual case. To discuss this assumption, one has to start from a more general relationship than equation 10, for instance:

$$\log \beta_i = -0.505(\alpha c)^{\frac{1}{2}} + B\alpha c + \cdots \tag{12}$$

While the individual constant B shows certain regularities, no theory has been developed which safely predicts the value of B.

With the approximation of $1 - \alpha = \beta_i^2 c/K$, following from equation 8 for small values of $1 - \alpha$ and c, the stoichiometric activity coefficient can be represented by

$$\ln \gamma = \ln \alpha + \ln \beta_i = -\beta_i^2 c/K - 2.303[0.505(\alpha c)^{\frac{1}{2}} - B\alpha c] \tag{13}$$

Within the approximation desired in this case, β_i and α in the coefficients of c may be replaced by unity, so that

$$1/K = 2.303B - [2.303 \cdot 0.505(\alpha c)^{\frac{1}{2}} + \ln \gamma]/c \tag{14}$$

However accurately the experimental quantity γ may be known, the dissociation constant can be derived from equation 14 only if the absolute value of the unknown coefficient B may be expected to be small compared with $1/2.303K$.

From the extensive survey of Prentiss and Scatchard (111) it can be concluded that for hydrochloric acid roughly $B = 1$, and that values of about this amount occur quite frequently. The basic assumption does not hold, therefore, for values of K larger or even close to $\frac{1}{2}$.

In the place of equation 10, more elaborate relationships have been used, which are likely to give somewhat better values for β_i. But the uncertainty in β_i is not so much reduced that the order of magnitude of the estimated limit of K is changed.

The situation is similar with respect to the methods which use Λ instead of γ for the determination of the dissociation constant.

For these reasons, calculations of dissociation constants of moderately strong electrolytes should always be critically examined. A cautious statement, incidentally made by this author (126) in 1930, that the freezing points of thallous nitrate solutions can be represented by (Debye's limiting law and) a dissociation constant $K = 0.80$, has no significance in spite of Nernst's (100) assertion that this salt is obviously not completely dissociated. The same is true for numerous dissociation constants calculated by Davies.

The upper limit for the derivation of dissociation constants from activity coefficients or conductivities is much lower for polyvalent electrolytes, owing to the lower range of validity of the limiting laws. For instance, even a dissociation constant as low as $K = 0.0045$ ascribed to zinc sulfate (27) is highly questionable (20, 21). The same is true for other similar cases.

The transference number, successfully used in early and recent times for the investigation of complex ions (see, for instance, 67a, 86, 140a), has been repeatedly used as a source of information regarding incomplete dissociation. However, the limitations applying to the conductivity are valid also for the transference number (*cf.* 46, 87).

While the promotion of our knowledge of dissociation was one of the great successes of the theory of Debye and Hückel, there still remained a large class of electrolytes of which no more could be said but that no evidence was available of the existence of undissociated molecules in dilute solutions.

VI. ION PAIR AND MOLECULE

Before we can proceed in reporting the various attempts made in recent times to investigate the dissociation of strong electrolytes, the concept of the undissociated molecule is to be discussed briefly. In the historical development of our problem some doubt has arisen as to whether or not a sharp distinction can and should be made between molecules in the traditional meaning and ions which are kept close together by strong electrostatic forces.

An early paper of A. A. Noyes (102), discussed in a preceding section, may perhaps be interpreted as suggesting that electrostatic attraction produces molecules of a particular character.

Bjerrum (11), in 1926, went a step farther. He noticed that, according to the theory of Debye and Hückel, under certain conditions an appreciable fraction of the ions must be very close to ions of the opposite sign, forming "ion pairs." Treating this association of ions to pairs formally like the formation of molecules, he developed an efficient approximation method for calculating the influence of the electric forces on the activity coefficient at moderate concentrations. This method was repeatedly used by other authors,—in an elaborate method by Scatchard and Epstein (135a) and by Fuoss (50) for non-aqueous solutions. Indeed, the electric forces acting in solutions of low dielectric constant are so great that a large fraction of the ions must be kept together quite firmly by Coulomb forces.

From another viewpoint Fajans (40, 42, 43) arrived at somewhat similar conclusions. He observed that the interaction manifested in the dependence of the molar refraction on the concentration furnishes proof of contact between ions and of the mutual deformation of their electronic systems. According to Fajans, pairs of rigid undeformed ions represent the extreme case of the ideal ionic bond. The variation of the molar refraction constitutes a measure of the deformation and, in general, of the approach to the non-polar bond type. All intermediate stages between these extreme types exist.

The old concept of the undissociated molecule obviously can be maintained only if a criterion exists which permits one to draw a natural and reasonably sharp line between molecules and interacting ions. This criterion must be theoretically significant and experimentally realizable.

A criterion of this kind is the vibration spectrum. In addition, the vibration spectrum affords an opportunity to maintain in a precise way the traditional idea of the molecule as a mechanical unit. In the days of the kinetic theory of gases this primary property of the molecule was so far beyond any doubt that it hardly was even discussed.

As a mechanical unit, a molecule or an ion possesses three translational degrees of freedom. The dissociation of a molecule does not change the total number of degrees of freedom, which is just three times the number of atoms. But it is accompanied by a change of three other modes of motion into translations. Also, the number of rotational degrees of freedom changes. It increases by three unless atomic or linear ions are involved. These special cases are easily examined one by one, the result being that on dissociation in any case at least one (type HCl) and at most six (type NH_4NO_3) modes of vibration change into translational or rotational motions.

The change of the number of vibrations, of course, need not be the only characteristic difference between the spectra of the molecule and the ions. It is especially the change of symmetry which causes characteristic and predictable changes in the vibration spectrum.

Very extensive experimental evidence supports the conclusion that the vibration spectrum is indeed a characteristic property of a molecule or ion. The environment influences the vibration frequency and the width of a spectral line, but the general type of the spectrum and the number of lines depend only on the nature of the molecule or ion.

Frequently, but not necessarily, the Raman spectrum presents sufficient information to enable one to distinguish between the molecule and the ions. However, in a case like solutions of sodium chloride the absence of a Raman line corresponding to the sodium–chlorine vibration cannot be taken for final evidence of complete dissociation, since the intensity of Raman lines correlated with polar bonds is always low.

On the other hand, the fact that the intensity of the nitrate lines in the Raman spectra of alkali nitrates is proportional to the concentration (116, 123, 139) furnishes sufficient proof of complete dissociation. The validity of this conclusion, of course, is restricted by the limits of experimental errors, which may amount to 5 per cent or even more. But the significance of this restriction need not be overestimated. Actually it applies only to the highest concentrations, i.e., to almost saturated solutions, since the fraction of undissociated molecules in any case must decrease with decreasing concentration.

These two examples illustrate the fact that each case must be discussed individually. But there can be no doubt that the question of dissociation can be solved in any case in which complete knowledge of the vibration spectrum is available.

It need hardly be pointed out that ion pairs are not molecules according to the suggested definition (123).

No logical objections are to be raised against a more extended definition of the term "molecule," which also includes ion pairs and interacting ions. In this case, however, a new term would be required for the traditional concept of the molecule. No advantage can be seen in abandoning the strictly definable meaning of an old idea and using the old term for a concept which cannot be sharply limited and does not require a separate term at all.

The statement that the proposed narrower definition of the molecule furnishes a strict distinction between molecule and ions is to be taken with a grain of salt. The average lifetime of a molecule as a mechanical unit may conceivably be of the order of magnitude of a vibration period. Experimentally this borderline case would be characterized by an anomalous width of a vibration line. No safe evidence of the existence of a case of this kind is available. The existence of borderline cases would not impair the usefulness of the concept.

VII. STRONG ELECTROLYTES

As mentioned in the preceding section, there is no reason to assume undissociated molecules even in concentrated solutions of some salts, such as the alkali nitrates. Many years ago, Bray (15) demonstrated that fused salts are dissociated to a high degree (*cf.* also 82), and later van Laar (144) and Gross (56) concluded that they are completely dissociated.

Never could there be any doubt, however, that concentrated solutions of some strong electrolytes contain a large fraction of undissociated molecules. The low conductivity of the absolute acids and the high amount of the heat of mixing and of the volume contraction on dilution furnish sufficient evidence. In addition, a reaction like

$$HClO_4 + H_2O = H_3O^+ + ClO_4^-$$

is necessarily incomplete if the molal ratio exceeds 1:1. Direct proof was furnished by the discovery of the Raman spectra of undissociated nitric acid (17, 74, 114, 151) and of other strong acids.

Various attempts at estimating dissociation constants or degrees of dissociation of strong acids (16, 38, 45, 60, 63, 100, 136, 137, 152, 154) were entirely unsuccessful. Obviously this failure was due to the direct or indirect introduction of the laws of the perfect solution. Two methods, however, appear to approximate the order of magnitude: Wynne-Jones (153) extrapolated the dissociation constants of non-aqueous solutions as a linear function of the reciprocal values of the dielectric constant, and Kossiakoff and Harker (77) based an estimate on the constitution of the molecule.

The classical methods failed because they were based on properties which are influenced too much by the environment of the ions and the molecules, and also because these properties are not sufficiently distinct for ions and molecules. Safe quantitative results for the degree of dissociation of a strong electrolyte could be expected only from a property which is highly characteristic of a particular ion or molecule, and at the same time is not seriously affected by its environment. Apparently only some optical properties and the magnetic susceptibility satisfy these requirements. Since A. A. Noyes's early remark (101), it has been realized by Lewis (80), Bjerrum (10), and Hantzsch (64) that the absorption of light promised to furnish a clue to the problem of dissociation. Likewise, the intensity of Raman lines furnishes quantitative and unambiguous information.

Precise refractivity measurements have been used by Fajans as a powerful tool to elucidate the mutual influence of ions. It was to be expected that the much coarser effect of dissociation is conspicuous also in the refractivity. This is confirmed by the example of nitric acid, discussed in a later section. The refractivity is less useful for a primary determination of the extent of dissociation, since in general all components of a solution contribute appreciably to its value.

Okazaki's measurements and review of older data (106) indicate a similar situation for the rotation of the plane of polarization in a magnetic field.

The magnetic susceptibility may be expected to furnish unambiguous quantitative information regarding the dissociation of some strong electrolytes (*cf.* 46).

VIII. ABSORPTION OF LIGHT

In many cases frequencies can be found for which the extinction coefficient of one of the ions is much larger than that of the molecule, or *vice versa*. In these cases the extinction coefficient is sufficiently specific.

The influence exerted on the extinction coefficients by the components of the solution was carefully examined by Halban and Eisenbrand (60). Their data and the results of Fromherz and coworkers (32, 33, 48, 49) show clearly that this influence, while definitely exceeding the limits of experimental error, is considerably smaller than the changes which frequently are produced by dissociation.

The extensive and accurate measurements of these authors demonstrate that a quantitative determination of degrees of dissociation and dissociation constants of strong electrolytes can be based on extinction coefficients.

Unfortunately, the available data are not quite sufficient for definite conclusions in this respect. The substances investigated by Fromherz either reveal no incomplete dissociation at all, like the halides of the alkali and alkaline earth metals, or are electrolytes of moderate strength (*cf.* table 1). The measurements on nitric acid and calcium nitrate by Halban and Eisenbrand do not furnish sufficient information on dilute solutions.

Dalmon's measurements (22) on nitric acid and the results of Freed and his coworkers (45a, 45b, 46a) for europium nitrate will be discussed later.

IX. RAMAN SPECTRA

For the reasons discussed in a preceding section, Raman spectra yield the most direct and conclusive evidence. As mentioned before, several authors (18, 114, 139) realized that the intensity of a Raman line is proportional to the concentration of the corresponding molecule or ion. But their attempts to determine the constant factor relating intensity and concentration were obviously unsuccessful.

According to a suggestion made by Redlich and Rosenfeld (127) in 1937, the true ionic concentration is determined by comparison with the solution of a completely dissociated electrolyte containing the same ion. Thus, to find the concentration αc of the ions in nitric acid of concentration c, one prepares a solution of sodium nitrate of such strength that the intensity of the Raman lines of the nitrate ion is equal for both solutions. Since sodium nitrate is practically completely dissociated, its stoichiometric concentration is equal to its ionic concentration or equal to αc. This method has been used by N. R. Rao (115, 116, 118, 120), Redlich and Bigeleisen (123), and Redlich, Holt and Bigeleisen (124).

The method not only eliminates the apparatus factor relating intensity and concentration but also has the technical advantage that only lines of equal intensity are to be compared. Still the experimental difficulties are considerable, owing to the fact that the Raman lines are broader in the presence of the acid molecules.

So far only the photographic method has been used. But owing to the peculiar relationship between light intensity and blackening, the photographic plate is a poor tool for integrating intensities distributed in different ways. In addition, owing to the comparatively low intensity, a considerable distortion of the distribution by the finite widths of the slits of the spectrograph and microphotometer can hardly be avoided. Even with an elaborate method of comparing intensities (124) the limits of error are still large. Important progress can be expected from the use of the photoelectric method, for which suitable equipment has been developed in recent years (112, 113).

The special results reported in the following sections are based primarily on the method of comparing the intensities of the Raman lines.

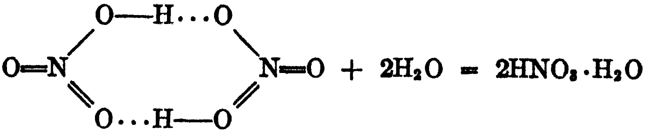
X. NITRIC ACID

The degrees of dissociation found by N. R. Rao (116) and by Redlich and Bigeleisen (123) are in good agreement. The latter authors derived the value $K = 21 \pm 4$ for the thermodynamic dissociation constant defined by equation 8.

This value agrees sufficiently well with Wynne-Jones' estimate $K = 40$ (153), with the value $\log K = 0.1$ of Kossiakoff and Harker (77), and with the value $K = 9$ derived by the author (122) from the extinction coefficients of Halban and Eisenbrand (60). It is just compatible with the lower limit derived by Halban and Seiler (61) by an indicator method.

The question of the molecular constitution of nitric acid has been the subject of many discussions. Today sufficient experimental data are available for a fairly detailed and reliable description.

Chédin (19) concluded from the Raman spectrum that the absolute acid contains a few per cent of nitrogen pentoxide, as already suspected by Halban and Eisenbrand (60). Dalmon and Freymann (24, *cf.* also 23) found evidence of hydrogen bonds in their infrared spectra. According to their spectra, addition of water results in depolymerization, which perhaps may be symbolized, as suggested by Hantzsch (64, 65), by the equation:



$$+ 2H_2O = 2HNO_3 \cdot H_2O$$

However, the existence of the dimer and the hydrate as definite molecules in the solution has not been directly proven.

TABLE 2

Degree of dissociation (α) *of nitric acid* (*approximately 25°C.*)

c	0.1	1	2	3	4	6	8	10	12	14
α	0.997	0.978	0.95	0.90	0.85	0.72	0.56	0.42	0.28	0.16

According to the infrared spectra, this reaction is practically complete at the composition corresponding to $HNO_3 \cdot H_2O$ ($c = 18$). At this concentration not more than a few per cent of the acid are dissociated (table 2). Dissociation takes place mainly on dilution from $c = 14$ to $c = 4$. The degree of dissociation for lower concentrations is best obtained by graphical extrapolation of log ($K\beta_u$) (123) and by means of equation 8. The approximate values recorded in table 2 for higher concentrations are taken from a smooth curve.

This picture of the molecular constitution of nitric acid, while not particularly precise in detail, is directly based on experimental facts. It is somewhat simpler than expected by earlier authors. The brilliant ideas which Hantzsch suggested on an experimentally and theoretically insufficient basis find a striking confirmation in some respects, while they fail entirely in other respects.

The dependence of many properties on the concentration has often been connected with the dissociation of strong electrolytes. Strangely enough, the attention was usually concentrated on dilute solutions, where the effect of dissociation is entirely negligible (*cf.* 100). Actually, several properties of nitric acid solutions change greatly just in the range between $c = 4$ and $c = 14$. These variations can be safely, and even in a crudely quantitative way, correlated with the dissociation. They are more or less clearly distinct from the variations which are due to other causes,—namely, depolymerization and hydration, responsible mainly at concentrations higher than $c = 18$, and ionic interaction, conspicuous in the dilute range. The electrostatic effects are always much smaller than the effects due to chemical changes.

The apparent molal volume, Φ, and the molal refraction, R, measured by Fajans and coworkers (39, 41, 75, 84), and the extinction coefficient, ϵ, at 3180 Å., determined by Dalmon (22), are plotted as functions of $1 - \alpha$ in figure 1.

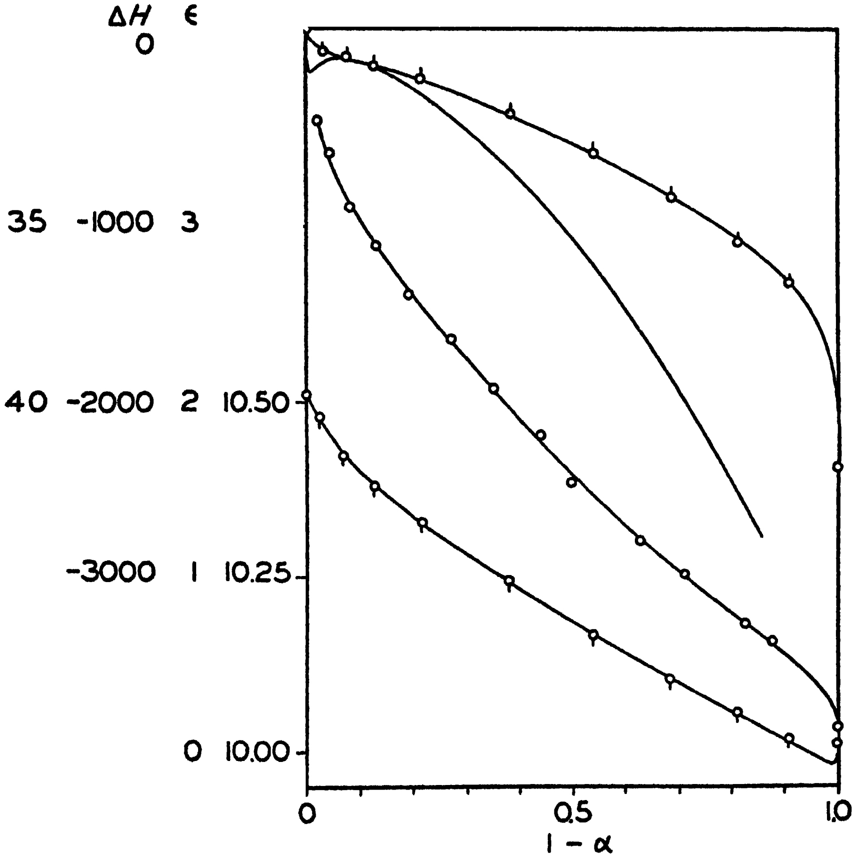


FIG. 1. Nitric acid. ȯ, apparent molal volume (Φ); ΔH, heat content per mole HNO_3; O, extinction coefficient (ϵ); ♀, molal refraction (R) as function of the degree of dissociation.

In a diagram like this any colligative property $g = g_i\alpha + g_u(1 - \alpha)$ is represented by a straight line. Actually, the three curves are fairly flat in the middle portion. This indicates that the variation in this range is mainly due to dissociation. It is quite possible that the remaining curvature is partly due to errors in the degree of dissociation. Crude values of the refractivities, extinction coefficients, and molal volumes of the ions and the molecule can be read from the diagram.

The integral heat of dilution, $-\Delta H$ (9, 70, 127), can hardly be considered a colligative property. From the slope of the curve in figure 1 one may estimate that the heat of dissociation will be in the range of about 2000 to 5000 calories per mole. This means that the heat of dilution of the absolute acid, 7440 calories, includes a considerable amount for depolymerization and hydration.

This estimate can be compared with a similarly crude value which may be derived from N. R. Rao's measurements (120) of the degrees of dissociation at higher temperatures (table 3). For each of the two lower concentrations the two temperature intervals furnish approximately equal values for

$$\frac{\mathrm{d}}{\mathrm{d}T} \ln \frac{\alpha^2}{1-\alpha} = \frac{\mathrm{H}_i - \mathrm{H}_u}{RT^2} - \frac{\mathrm{d}}{\mathrm{d}T} \ln \frac{c\beta_i^2}{\beta_u} \tag{13}$$

where the molal heat contents of the ions and the molecule are denoted by H_i and H_u. Neglecting the last term in equation 13, one obtains $\mathrm{H}_u - \mathrm{H}_i = 2400$ and 4500 for $c = 10.5$ and 12.58. The two temperature intervals do not furnish consistent values for $c = 14.50$.

Another check of the order of magnitude can be carried out by means of Miščenko's data for the specific heat (96), which agree well with unpublished measurements by Rosenfeld (131). In the concentration range, which is most affected by the change of dissociation, the specific heat can be approximated by

TABLE 3

Degree of dissociation of nitric acid at higher temperatures

c	10.5	12.58	14.50
30°C	0.352	0.212	0.114
60°C	0.300	0.155	0.095
90°C	0.226	0.105	0.032

$$c_p = (1-p)c_0 + p[\alpha c_i + (1-\alpha)c_u + (\mathrm{H}_i - \mathrm{H}_u)\mathrm{d}\alpha/\mathrm{d}T] \tag{14}$$

where p denotes the grams of nitric acid dissolved in 1 g. of the solution, and c_0, c_i, and c_u the specific heats of water, the ions, and the molecule, respectively. The quantity $\mathrm{d}\alpha/\mathrm{d}T$ is eliminated by means of equation 13, the last term again being neglected. Denoting the molal weight of HNO_3 by M, one obtains:

$$c_p = c_0 + p\left[c_i - c_0 + (c_u - c_i)(1-\alpha) + \frac{\mathrm{H}_i - \mathrm{H}_u}{\mathrm{M}RT} \cdot \frac{\alpha(1-\alpha)}{2-\alpha}\right] \tag{15}$$

Table 4 contains Miščenko's values for 21.07°C. and the values calculated with $c_0 = 0.9983$, $c_i = -0.115$, $c_u = 0.435$, and $\mathrm{H}_i - \mathrm{H}_u = 3300$. The agreement, while quite satisfactory, is not very significant, as three arbitrary coefficients have been introduced. But it may be noted that the values of c_i and c_u are reasonable, and that the value of $\mathrm{H}_i - \mathrm{H}_u$ agrees with the two preceding estimates.

This interpretation of the variation of all these properties is undoubtedly very crude, but it furnishes a consistent and fairly simple picture.

XI. NITRATES

According to numerous measurements the Raman spectrum of aqueous solutions of all nitrates contains a moderately strong line at about 720 cm.$^{-1}$ (*cf.* 93). In the spectrum of concentrated solutions of polyvalent nitrates an additional line appears, the frequency of which is about 20 cm.$^{-1}$ higher. The interpretation of this line as due to an intermediate ion such as $CaNO_3^+$ etc. has been discussed, though not generally accepted, by several authors (25, 26, 55, 79, 107, 108, 130).

Bauer, Magat, and Da Silveira (8) tested this interpretation by comparing the intensities of the two lines with the intensity of the strong nitrate line at 1050 cm.$^{-1}$ in solutions of calcium nitrate and of mixed solutions of calcium nitrate with calcium chloride and lithium nitrate. The results did not agree with what was qualitatively expected according to the mass-action law. However, Bauer, Magat, and Da Silveira undoubtedly overestimated the applicability of the photographic method of measurement of intensity. The two lines in question are so close that they can hardly be sufficiently resolved in a determination of intensities, and the line at 1050 cm.$^{-1}$ is so much stronger that it cannot be used as a reference. In fact, unpublished results of Mr. I. I. Friedman (47) on solutions of calcium nitrate and chloride are qualitatively in perfect agreement with the mass-action law.

TABLE 4

Specific heat of nitric acid at 21.07°C.

p	c_p (OBSERVED)	c_p (CALCULATED)	p	c_p (OBSERVED)	c_p (CALCULATED)
0	0.9983		0.35	0.7371	0.7344
0.06	0.9286	0.9336	0.40	0.7175	0.716
0.10	0.8861	0.8932	0.45	0.6992	0.701
0.15	0.8426	0.8474	0.50	0.6815	0.683
0.20	0.8063	0.8097	0.55	0.6622	0.665
0.25	0.7790	0.7791	0.60	0.6415	0.647
0.30	0.7576	0.7535	0.65	0.6190	0.625

A similar split into a doublet has been observed with regard to the diffuse lines at 1350 cm.$^{-1}$ (all nitrates) and 1450 cm.$^{-1}$ (only polyvalent nitrates). Both lines, however, appear also in Friedman's spectra of sodium nitrate and lithium nitrate, the relative intensity of the higher frequency being greater in solutions of polyvalent nitrates. These results have not yet been explained.

Similar though less extensive evidence is available for many bivalent and trivalent nitrates.

The results of Freed and coworkers (45a, 45b, 46a) present, as far as this reviewer can see, unambiguous evidence for the incomplete dissociation of europium nitrate. Europium salts are exceptional in having sharp absorption lines in the blue region of the spectrum. Freed found four absorption lines with nitrate solutions at $c = 0.0007$, identical with lines of europium chloride in solutions up to $c = 1.5$. However, between $c = 0.01$ and $c = 1.5$, three lines were found for the nitrate, at least one of which is clearly different from the chloride lines. In the middle range,—namely, between 0.001 and 0.01,—superposition of both spectra was found.

This is precisely the behavior to be expected if $Eu(NO_3)^{++}$ is a weak electrolyte. While a closer examination of the thermodynamic properties is desirable, there is no reason to expect any results inconsistent with the theory of Debye and Hückel, since appreciable deviations from the limiting laws must be anticipated for a trivalent electrolyte even in the range from 0.001 to 0.01 with or without complete dissociation.

XII. PERCHLORIC ACID

A comparison of the results obtained for nitric acid and perchloric acid reveals the wide differences which exist within the group of strong electrolytes. The degrees of dissociation from Raman data (124) substantiate the assumption of earlier authors, especially of Hantzsch and Weissberger (66), that this acid is considerably stronger than nitric acid. While some of the figures of table 5 may be in error by as much as 10 per cent, some characteristic differences are quite obvious. The maximum ionic concentration of nitric acid amounts to 4.5 gram-ions per liter (at $c = 7.5$), that of perchloric acid to 10.3 (at $c = 12$). At the composition of the monohydrate, nitric acid is practically undissociated; the degree of dissociation of perchloric acid is about 0.55 ($c = 14.7$). At high concentrations the dissociation of perchloric acid appears to approach completeness with respect to the reaction:

$$HClO_4 + H_2O = ClO_4^- + H_3O^+$$

TABLE 5

Dissociation of perchloric acid

PER CENT	c (25°C.)	αc (53°C.)
60	9.1	8.9
70	10.9	10.1
	12.0	10.3
84.8	14.7	8.1
	16.0	5.6

The dissociation increases considerably with decreasing temperature. This is in accord with the large heat of mixing.

The available experimental data do not indicate any molecular species other than the ions and the undissociated acid. The dissociation constant could not be calculated, because the activity coefficients are known only in the range of practically complete dissociation.

N. R. Rao (121) found an appreciable change of the intensity of the line at 930 cm.$^{-1}$ when he compared spectra of perchloric acid in the range between $c = 5$ and $c = 10$ obtained with exposures inversely proportional to the concentration. The actual change of dissociation in this range amounts at most to a few per cent at room temperature and is undoubtedly far below the limits of perceptibility in this method. The apparent change in intensity illustrates the well-known fact that misinterpretation of photographic intensities can be avoided only by a careful technique.

XIII. OTHER SUBSTANCES

Sulfuric acid was investigated by N. R. Rao (115) by comparison with ammonium sulfate and potassium hydrosulfate. Rao's table of his results contains several inconsistencies, and this author has not been able to derive satisfactory figures. De Béthune and Kimball (30) attempted to locate one error and calculated concentrations of the hydrosulfate ion.

Ochs, Guéron, and Magat (105) found a diffuse Raman line at 2630 cm.$^{-1}$ in hydrochloric acid above $c = 9$. At this concentration, therefore, an appreciable fraction of undissociated molecules must be present.

A few measurements on iodic acid were made by N. R. Rao (118). The same author (117) also found that dissociation decreases with increasing temperature, a fact which can be immediately derived from the positive sign of the heat of mixing. Rao also found (119), obviously by a misinterpretation, some qualitative contradiction to the expected common-ion effect.

XIV. CONCLUSIONS

So far only the measurement of the intensities of Raman lines has furnished unambiguous quantitative results. But extinction coefficients and magnetic susceptibilities are also so characteristic of the molecular state that independent results may well be expected.

Various properties like refraction, volume, heat content, and heat capacity indicate the influence of dissociation clearly enough. Since they are less specific they can, however, hardly furnish primary quantitative information.

In the interpretation of Raman spectra it should be always borne in mind that the absence of a characteristic spectrum is not a conclusive proof of the absence of a molecule. The specific intensities of Raman lines are so widely different that complete dissociation can be demonstrated only by the determination of the intensities of the lines of the ions.

At present only a small amount of information on the dissociation of strong electrolytes is available. Moreover, the accuracy of the data is low. But there is little reason to doubt that more extensive and more accurate information can be obtained, and that coördinated examination of various properties will furnish opportunities to check the results. One of the old problems of physical chemistry appears to be on the way toward solution.

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APPLICATION OF LOW TEMPERATURES TO CHEMICAL RESEARCH[1]

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The important physical-chemical investigations which have been carried out at temperatures below 0°C. are reviewed from the point of view of special methods involved, and in order to facilitate reference to the literature. An extensive bibliography is given.

The work has been arranged under the following headings:—the measurement of temperature; cryostats; crystallization and distillation at low temperatures; boiling point; melting point; density; dielectric constant; heat capacity; heats of fusion, transition, and vaporization; phase equilibria; adsorption of gases on solids; other physical properties.

I. INTRODUCTION

Many fields of physical chemistry have been advanced by studies made below the melting point of ice. The investigations have sufficient in common to make it desirable to review them together. This has been done briefly in the present article, mainly with the object of acquainting the reader with the special methods employed and facilitating reference to the literature by those commencing investigations at temperatures below 0°C.

In some cases it has been necessary to include elementary or well-known theory in order to make clear the object of certain studies,—for example, those on dielectric constant.

While the literature has been covered up to December, 1944, no attempt has been made to make the bibliography complete.

II. THE MEASUREMENT OF TEMPERATURE

A. Gas thermometer

It goes without saying that the fundamental method of measuring low temperatures is by gas thermometry. This subject has been discussed thoroughly by Keesom and Tuyn (117), and many convenient gas thermometers have been described (19, 23, 30, 73, 102, 115, 119, 126).

Fortunately, it is never necessary to use the gas thermometer to measure temperature directly. Instead, the readings of a secondary thermometer are andardized against a gas thermometer and the calibrated instrument is used subsequent work.

inte.

B. Vapor-pressure thermometer

by a vapor pressure of a substance is a highly sensitive temperature indicator.
coincide of oxygen near its boiling point the vapor pressure increases 1 mm.
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to absolute
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to solve for

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[1] the Symposium on Low-Temperature Research which was held under the ivision of Physical and Inorganic Chemistry at the 109th meeting of the l Society, Atlantic City, New Jersey, April, 1946.

[2] um Company Fellow.

per 0.013° rise in temperature. For a substance which boils below room perature it is merely necessary to introduce it (sufficient to be sure that the liquid) into an evacuated bulb connected to a manometer (94, 123). The l must be the coldest part of the system. As a check on the purity it is advis to take the vapor pressure after various fractions of the liquid have been tilled off.

It is necessary that the tube leading to the vapor-pressure bulb be prote from the surface of the cryostat if there be any chance of its being colder t the vapor-pressure bulb. This can be accomplished best by surrounding tube with a vacuum jacket (94).

A small compact vapor-pressure thermometer has been described by Far and Farkas (65).

The vapor pressures of hydrogen, oxygen, and carbon dioxide are the ba of reproducible fixed points on the temperature scale. It is customary to ta readings near the normal boiling point of the substances and to calculate fr them and report the normal boiling point (the temperature where the vap pressure would be 760 international millimeters of mercury). (See, for examp reference 94.)

C. *Liquid-in-glass thermometer*

This type of thermometer has been extensively used and was developed b Timmermans (243) for work on the properties of organic compounds at lo temperatures. If properly constructed of strain-free glass such thermomete are reliable to 0.1°. Toluene can be used as the liquid down to −95.1°C., whil normal pentane can be used down to −131.5°C. and isopentane down t −159.7°C. Such thermometers are usually calibrated against a secondar standard such as a platinum resistance thermometer.

D. *Thermocouple*

The most commonly used thermocouple for temperatures down to −260°C. is copper–constantan. For the so-called Advance (constantan) wire of Driver–Harris against copper, reference tables have been given (19, 73, 202, 225).

For work down to liquid-air temperatures, if an accuracy of only 0.2° is required, it is sufficient to calibrate such a thermocouple against the boiling point of oxygen and the sublimation point of solid carbon dioxide (202). The condition for such a method to be valid is that the deviation in microvolts from th reference tables be nearly proportional to the electromotive force of the coup This condition is generally fulfilled, so that temperatures can be calculated the reference tables and a deviation graph. For more accurate work, co son against a resistance thermometer or directly against a gas therm advisable. At liquid-air temperatures, and above, such thermocou their original calibration to a few hundredths of a degree (18).

For work below liquid-air temperatures direct calibration agai mometer is advisable, and the original calibration should be fre against fixed points (e.g., triple and boiling point of hydroge and melting point of oxygen). Deviations from the original calibration of 0.4° at the hydrogen triple point have been known to develop after extended use (18). If such deviations are detected and a correction applied, the copper–constantan thermocouple is a satisfactory thermometer down to the triple point of hydrogen.

E. Resistance thermometer

Resistance thermometers of platinum (35), platinum–rhodium (30, 228), and gold (116) with a trace of silver added (76) have been used from room temperature down to liquid-hydrogen temperatures. Copper resistance thermometers have also been used (77). Below −245°C. constantan (118) and below −265°C. phosphor-bronze (113) are suitable for resistance thermometers. For accurate work it is necessary to calibrate such instruments against a gas thermometer, with one single exception—the platinum resistance thermometer which is the basis of the international temperature scale (35).

A resistance thermometer of pure platinum between 0°C. and −183°C. obeys the equation

$$R_t/R_0 = 1 + At + B_t^2 + C(t - 100)t^3 \qquad (1)$$

where R_t/R_0 is the ratio of the resistance at the Centigrade temperature t to that at the ice point, while A, B, and C are constants. The international temperature scale below 0°C. is defined by assigning values to the boiling point of oxygen (−182.970°C.) and the boiling point of sulfur (444.60°C.), which were the best available values on the perfect gas scale. The freezing point and boiling point of water are respectively taken as 0° and 100°C. The constants A and B are evaluated by measuring R_t/R_0 at the boiling points of sulfur and water (for technique see references 21, 22, and 114). In defining the temperature scale in the range of 0–444.60°C., the last term of equation 1 is not included but the same constants are retained. Therefore, the last term is omitted during the solution for A and B. The constant C is obtained by taking readings in a bath of boiling oxygen (for technique see references 115 and 202).

If it is not convenient to heat the thermometer above the ice point, the sublimation point of carbon dioxide and the freezing point of mercury may be used to replace the steam and sulfur points. These points have been established as secondary points on the international temperature scale (see reference 94). Once the constants have been obtained for a pure platinum thermometer, equation 1 yields temperatures on the international scale. The object was to have the international scale agree with that of a perfect gas.

Measurements at Leiden (115) and at the Reichsanstalt (95) indicate that the international temperature scale lies below the thermodynaimc Centigrade scale by a maximum of 0.04° at −80°C., while at the boiling point of oxygen the two coincide to within the experimental error (0.01°). No value of the ice point on the absolute scale was recommended for converting international temperature to absolute temperatures. To convert the international temperature scale to the absolute thermodynamic scale as used in a particular laboratory, it is best to solve for C of the resistance thermometer equation, using the Centigrade temperature for the boiling point of oxygen on the scale of that laboratory. To the temperature calculated using this value of C, the value of the absolute thermodynamic temperature of the ice point (on the scale of that laboratory) should then be added.

In defining the international temperature scale it was specified that the entire section of the thermometer at the measured temperature be of pure platinum and that the wire be wrapped in such a way as to eliminate strain. Furthermore, it is stipulated that:

$$R_{100°C}/R_{0°C} > 1.39, \qquad R_{444.60°C}/R_{0°C} > 2.645, \qquad R_{-183°C}/R_{0°C} < 0.25$$

Suitable platinum resistance thermometers are now supplied by several instrument makers (for their construction see references 114, 131, and 211) and a highly convenient resistance thermometer of the strain-free type has been designed by Meyers (159), the over-all dimensions of which are 5 mm. x 2 cm. Such thermometers can be put in a glass tube the size of an ordinary mercury thermometer or inside a short platinum case (5 x 45 mm.) (see reference 228) and the leads taken through a soft-glass cap. Such a thermometer, typical of several in use in this laboratory, is shown in figure 1. In this figure the cross with the platinum wire wrapped on is shown inside a glass case.

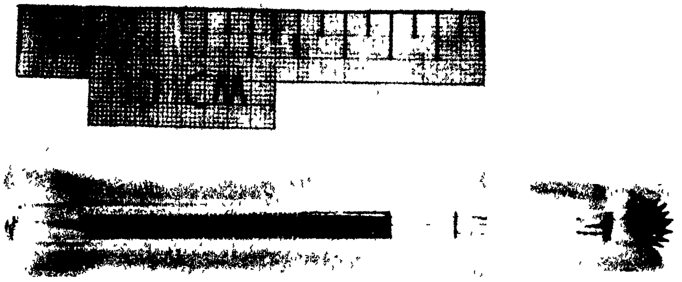

Fig. 1. Resistance thermometer

For the calibration to be permanent any of the resistance thermometers mentioned above should be so constructed that the wire is wrapped free from strain. Occasionally, it is necessary to wrap resistance thermometers directly on the outside of a calorimeter, but in this case they should be calibrated during each run against a thermocouple (76) or a strain-free resistance thermometer.

III. CRYOSTATS

For physical measurements at low temperature it is necessary to have some device to keep the temperature constant. A list of the most important types of cryostat with a brief description follows:

(*a*) A stirred bath of some liquid with a very low freezing point, for example, pentane, is kept in a Dewar. The pentane is cooled by the addition of liquid air, or some other refrigerant. The liquid air should never be added directly, as explosions are almost certain, but rather to a copper vessel dipping into the pentane. Stock (231) has devised an ingenious apparatus for this purpose, which consists of a heavy ring of copper with a chamber for liquid air forming a segment of the ring. The ring fits closely around the upper part of the Dewar and has two loops of copper strip fastened to it which hug the sides of the Dewar (see figure 2). The whole is submerged in the bath liquid, which can be stirred.

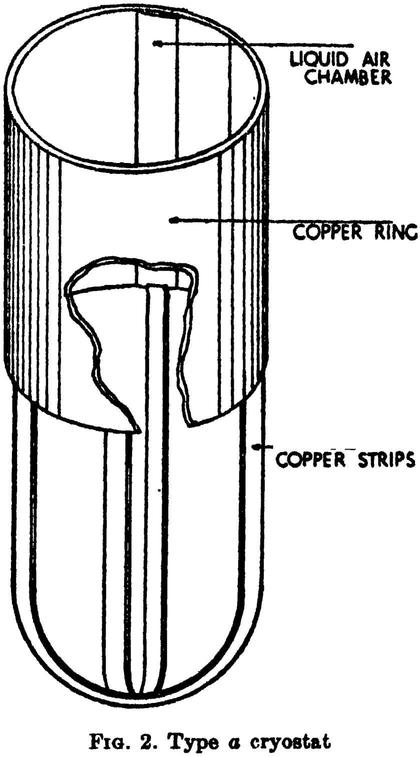

Fig. 2. Type *a* cryostat

Such cryostats have, of course, a slowly rising temperature but measurements good to a few tenths of a degree may be obtained with them.

(*b*) If a temperature range is not required, a series of liquids in equilibrium with the solid at the freezing point may be used in the cryostat of type *a* and thus very constant temperatures may be attained.

(*c*) In a somewhat more elaborate form of the liquid cryostat, capable of maintaining temperatures constant to 0.01°, the liquid is contained in a Dewar vessel with a stopcock connection to the vacuum space which allows the pressure in this space to be controlled (242). This Dewar is immersed in a second Dewar which contains the refrigerant (generally liquid air). The cryostat liquid is mechanically stirred. Its temperature may be controlled by adjusting the pressure between the walls of the inner Dewar. In some cryostats of this type, the pressure is kept sufficiently high to produce a general tendency to cool which is balanced by a heater in the bath (236). Such a cryostat is shown in figure 3. The heater can be operated manually, but more often it is automatically regulated. For automatic regulation bimetallic regulators have been used (108, 123), or a photoelectric regulation device is attached (225) to the galvanometer of a potentiometer. The potentiometer balances the electromotive force of a sensitive thermocouple (generally copper–constantan), or that across a resistance thermometer, with a constant current, which registers the bath temperature. If this rises, the galvanometer mirror directs a beam of light onto the photoelectric cell whose current then shuts off the heater. When a resistance thermometer is used, the galvanometer is sometimes placed in a bridge circuit containing the thermometer in one arm. A cryostat based on these principles has been designed by Scott and Brickwedde to give a constancy of 0.002° (115, 203). The particular feature of this cryostat is a very efficient system of stirring.

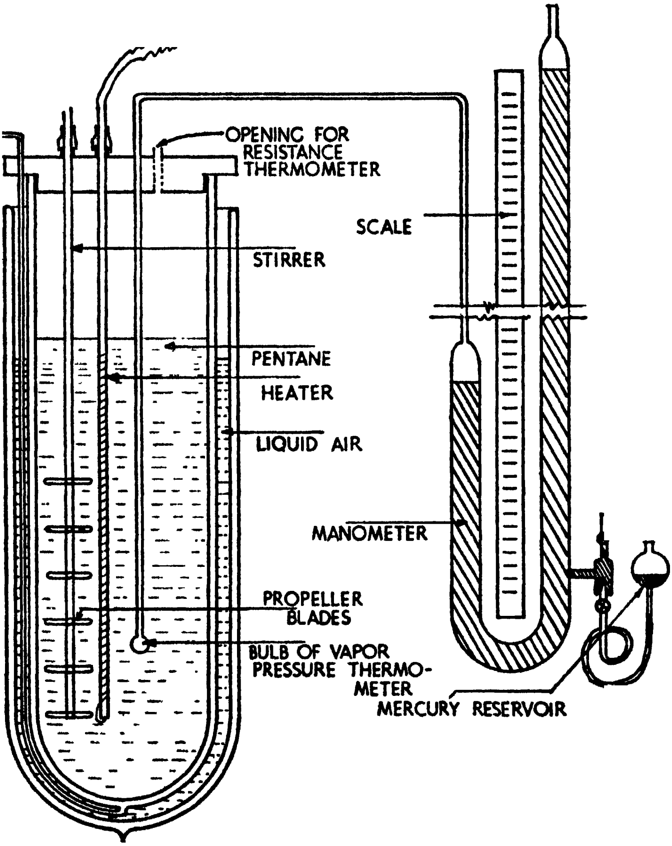

Fig. 3. Type *c* cryostat

When liquid air is used there is the danger that breaking of the inner Dewar may let the pentane into the liquid air, thus producing an explosive mixture. Southard and Andrews (225) use a copper tube to contain the pentane, and their heater is wrapped around the outside of this tube, which fits the Dewar closely. A convenient modification of this cryostat (126, 127) automatically controls the vacuum in the walls of the Dewar between the refrigerant and the bath by means of a solenoid valve controlled by a reversible Telechron motor operated by the same relay which shuts the intermittent heater on and off.

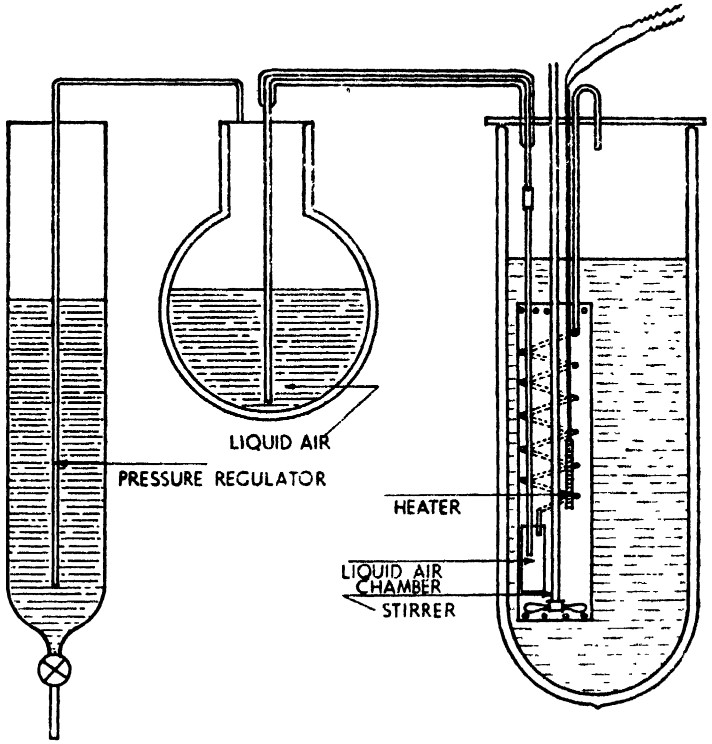

FIG. 4. Type *d* cryostat

(*d*) Liquid cryostats can also be maintained at constant temperature by controlling the amount of refrigerant supplied (146). Pentane or some other low-freezing liquid is contained in a Dewar. Liquid air is added slowly to a small copper vessel. The evaporation of the liquid air keeps the pentane cool. By controlling the rate of addition of liquid air and stirring, temperatures constant to 0.1° can be obtained.

Walters and Loomis (274) have brought such a cryostat to a high degree of precision. Their apparatus is shown in figure 4. They use good mechanical stirring and force the liquid air into the chamber through a vacuum-jacketed tube by pressure in the storage vessel. The pressure is controlled, by passing the evaporated air through a column of water (91), so as to supply enough liquid air to produce a general tendency to cool. This cooling is balanced by a hand-regulated electrical heater. A constant temperature of 0.01° for 3 hr. can be obtained using this cryostat. Instead of using the electrical heater it is possible to control automatically the supply of liquid air to obtain a constancy of 0.02–0.05°. The regulator is a vapor-pressure thermometer with a manometer which makes an electrical contact at a fixed pressure. Thus a solenoid escape valve is closed in the compressed-air supply to the liquid-air storage vessel. Pressure can

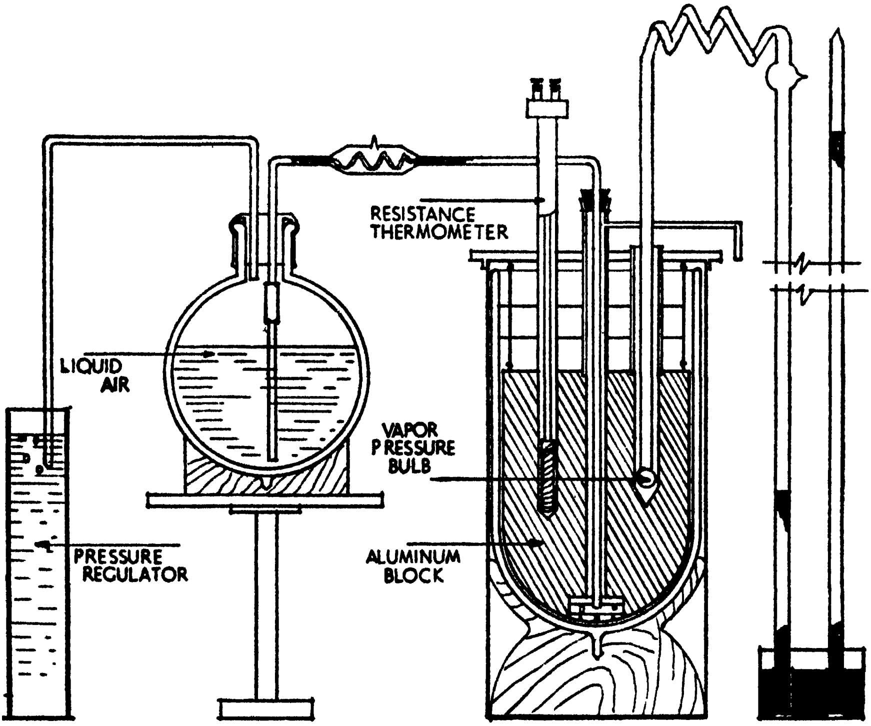

FIG. 5. Type *e* cryostat

thus build up and blow liquid air into the cooling chamber of the cryostat (144, 287). A regulated stream of cold air passing through coils in the cryostat can be used instead of liquid air. The air is cooled by passing through liquid air and its temperature regulated by combining with a stream of warmer air (51, 187). The air after cooling can be heated by an electric furnace regulated by a thermoregulator (68).

(*e*) A cryostat primarily for use in vapor-pressure measurements has been designed by Henning and Stock (92). It consists of an aluminum block machined to fit inside a Dewar vessel. Holes are drilled for two vapor-pressure bulbs and two resistance thermometers. A vacuum-jacketed tube leads from a liquid-air reservoir to a hole down the center of the block. The temperature of the block is regulated by controlling the rate of addition of liquid air to the hole. This is accomplished by regulating the pressure on the liquid-air storage Dewar by evaporation through a column of water. The apparatus is illustrated in figure 5. The vapor-pressure bulbs can be easily exchanged. Temperature can be maintained constant to 0.02° for half an hour.

In connection with low-freezing liquids for cryostats it is worth noting that a mixture of 5.8 cc. *n*-pentane, 2.2 cc. methylcyclohexane, and 1 cc. normal propyl alcohol is liquid and fairly fluid down to $-180°C$. (24).

IV. CRYSTALLIZATION AND DISTILLATION AT LOW TEMPERATURE

Purification of simple organic compounds which are gases at ordinary temperature and for which no chemical method is available must be effected by means of low-temperature fractional crystallization or distillation, while the purification of substances which are liquids at ordinary temperatures by recrystallization requires low-temperature technique.

The methods of fractional crystallization at low temperatures have been sadly neglected until recently. Indeed, it is for this reason that substances which are liquid at ordinary temperatures, and which seem to be pure as indicated by a constant temperature of distillation, yield such a variety of values for their freezing points as determined by different investigators. Such compounds have usually been purified by distillation which, in general, is not as satisfactory as recrystallization.

It is hoped that in the near future the subject of crystallization below room temperatures will be given more attention. Already the group at the National Bureau of Standards, while working on the isolation of the hydrocarbons from a midcontinent petroleum (275), has developed methods for the crystallization of hydrocarbons from mixtures. Miss Hicks (96) completely froze solutions of the hydrocarbon mixtures and placed the solid in vacuum-jacketed funnels. As the solid melted, with stirring, the liquid was drawn off from time to time.

Leslie and Schicktanz (139) froze the liquid mixture to a slush with vigorous stirring in a cylindrical funnel with a gauze bottom covered by a plate. Carbon dioxide snow and ether or liquid air were used as external baths for cooling. After freezing, the plate covering the gauze was removed and the unfrozen liquid drawn off by suction. In another apparatus the gauze bottom was omitted and the liquid removed by suction through a tube dipping to the bottom of the vessel and fitted with a filter plate at its lower end.

Hicks-Bruun and Bruun (97) have developed a low-temperature centrifuge which was used to purify heptane and methylcyclohexane obtained from gasoline. In this case, the material was completely frozen with vigorous stirring in a cylindrical vessel. The mush was transferred to the centrifuge by a method which eliminated moisture. The centrifuge was a rotating drum with perforated walls lined with fine linen. The liquid centrifuged out through the cloth collected in an outer housing which was surrounded by a bath of carbon dioxide slush. The liquid could be drawn off from the housing.

Leslie (138) has developed an apparatus for the crystallization of hydrocarbon mixtures by pouring their propane solutions into liquid methane. The crystals are separated by the use of a low-temperature centrifuge. For details of the ingenious apparatus the original paper should be consulted.

It is also worthwhile to mention the solvent dewaxing of lubricating oils at temperatures below 0°F. (110, 151). The oil is dissolved in a solvent such as naphtha, ethylene dichloride, trichloroethylene, propane, or benzene–acetone mixtures and chilled to −20°F. The waxes which separate are removed either by filtering or by centrifuging.

Fractional distillation through a column below room temperature differs from that above room temperature in the respect that it is more difficult to make a column adiabatic when heat has to be kept out than when it has to be kept in. Heat can be kept in by an easily controlled heated jacket at the same temperature as the column, whereas a cooled jacket is required to keep heat out—and this is not easy to control. The difficulty is solved by entirely vacuum jacketing the apparatus, and this procedure is followed in most modern columns.

The literature on low-temperature columns has been reviewed by Podbielniak (176) and by Rose (186). Podbielniak (177) has discussed thoroughly the effect of packing on column efficiency as well as the design and efficiency of vacuum jackets and Dewar vessels.

Low-temperature distillation has been used for analysis (169, 177, 178, 206, 209, 283) of low-boiling petroleum fractions as well as for their separation (31). Sometimes the column is surrounded by a separate and closely fitting vacuum jacket and sometimes it is sealed into a vacuum jacket. A reflux condenser at the top of the column keeps the column wet and supplies refrigeration.

Columns have been operated on total and partial reflux. In the former case, where the gas is withdrawn below the reflux condenser, the pressure can be kept constant by leaving the top of the column open to the air or open to a gas holder of hydrogen. In the case of partial reflux the gas is taken off at the top of the condenser and the entire apparatus is filled with the vapors of the substance being distilled. The coldest part of the apparatus controls the pressure, so that it is necessary to adjust the temperature of the condenser according to the rate at which gas is being withdrawn at the top of the column. This is done by adjusting the supply of refrigerant. When the refrigerant is liquid air, this can be done automatically (178). A manometer is attached to the top of the column. When the pressure gets too high the mercury in the manometer makes contact in a circuit which opens a solenoid valve and applies air pressure to the liquid-air container. Liquid air is blown into the condenser until the pressure falls and contact is broken. An alternative procedure is to cool the condenser with a stream of cold air passing through coils. The solenoid valve allows the current of cold air to pass or shuts it off. Either procedure can be applied to a total reflux column where an inert gas is not used. Figure 6 shows a diagram of our laboratory low-temperature column which operates on this principle. This column is packed with glass helices. It is used for the purification of simple organic compounds which boil below room temperature and whose physical properties are being studied.

Simons has described simple columns for the same purpose (209).

In connection with the separation of the chemical individuals from a mid-continent petroleum oil (see above), methods have been worked out for continuous counter-current extraction with low-boiling solvents (137). One apparatus is of glass and another of metal.

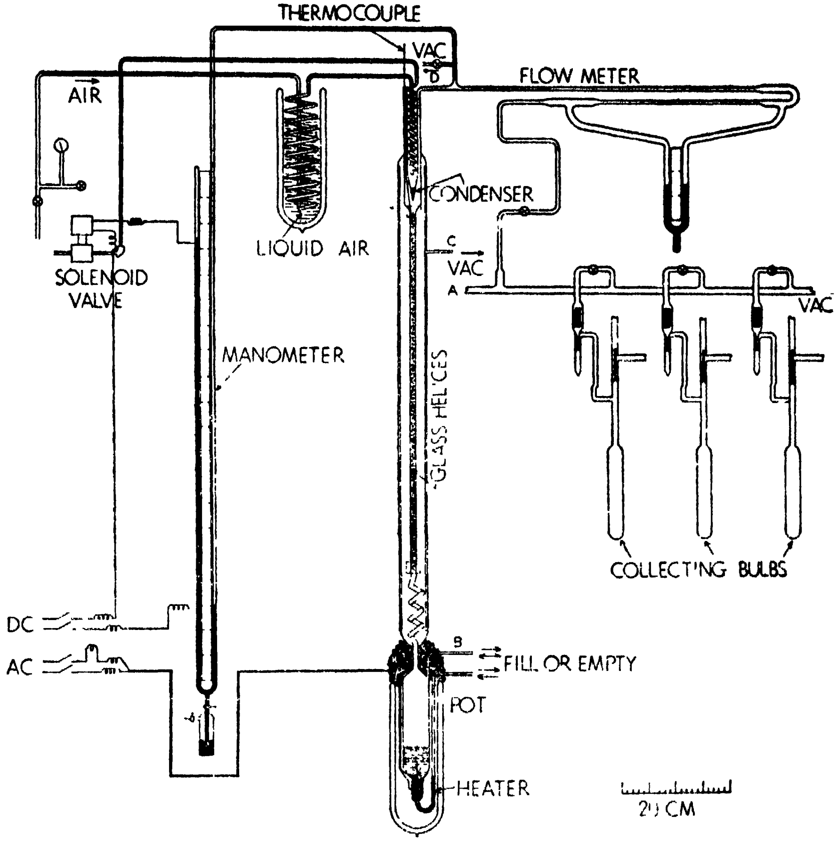

FIG. 6. Low-temperature column

V. BOILING POINT

For substances boiling below room temperature the accurate determination of boiling point is greatly simplified. The substance is placed in the bulb of a vapor-pressure thermometer as described above (94, 123). The vapor-pressure measurements are usually made against a thermocouple or resistance thermometer. A cryostat of type *c* (see figure 3) (123, 236) or type *d* is generally used (see figure 4) (146, 147, 274). In figure 5 the bulb of a vapor-pressure thermometer is located in the cryostat and shown connected to a manometer. With such an arrangement, it is possible to obtain results with an accuracy in temperature of 0.01°. From the results the normal boiling point can be calculated.

In recent calorimetric investigations on condensed gases and low-boiling liquids which will be discussed presently (Section IX), a tube from a manometer leads to the calorimeter so that the vapor pressure of the substance within can be measured. Either a thermocouple or a resistance thermometer fastened to the calorimeter measures the temperature. The calorimeter is surrounded by a radiation shield whose temperature can be controlled so that there is no heat transfer by radiation across the high vacuum in the chamber which holds the entire apparatus. The tube to the calorimeter makes an intimate contact with the top of the radiation shield, whose temperature is kept a few hundredths of a degree hotter than the calorimeter. In this way the temperature of the calorimeter never drifts more than 0.01° during a vapor-pressure measurement which takes about 10 min. This drift is a continuous function of the time. The average temperature of the calorimeter is known to a few thousandths of a degree and the average pressure to the same degree of accuracy. If the substance is pure, boiling points may be calculated from the vapor pressures to a few thousandths of a degree, providing the accuracy of the temperature scale warrants it. It is believed that this method at least rivals any other in precision and accuracy.

An extremely ingenious apparatus for determining vapor pressures has been devised by Francis and Robbins (71) for the determination of the vapor pressures of propane and propylene. It consists of a capillary-tube manometer whose closed end contains air and whose open end is attached to a small bulb containing the sample, confined by mercury. The bulb is easily filled. The readings of the manometer give the vapor pressure, after adding the pressure of the air on the closed side (calculated from the filling pressure and the volume not filled with mercury).

In table 1 are given the boiling points and melting points of some organic compounds which boil below room temperature; these points are known to an accuracy of a few tenths of a degree.

Where the previous determinations are discussed fully in the reference given, these are not usually included in the table.

VI. MELTING POINT

In the determination of melting points of organic substances which are solids only at low temperatures, Timmermans has been a pioneer. For his early work (243, 245, 246) he used pentane thermometers which had been previously calibrated against a platinum resistance thermometer. His method was that used in determining freezing points by the Beckmann method. About 10 g. of the material was partly solidified to a mush of crystals and liquid by slow cooling with vigorous stirring in a tube immersed in an air bath surrounded by the refrigerant (solid carbon dioxide and acetone or liquid air). The temperature of the stirred equilibrium mixture was then read on the pentane thermometer (of suitable range) and a stem correction made. This method (hereafter referred to as method I) has been claimed to yield results accurate to 0.1°, but this claim has not been substantiated.

When only a small quantity of material was available, a little was sealed in a capillary tube and frozen by liquid air. The tube was then attached to a pen-

TABLE 1

Melting and boiling points of simple organic compounds

COMPOUND	MELTING OR TRIPLE POINT	REFERENCE	NORMAL BOILING POINT	REFERENCE
	°C.		°C.	
Methane	−182.5	(39)	−161.37	(92)
	−182.47	(72)	−161.61	(123)
	−182.6	(63)		
Ethane	−183.23	(281)	−89.0	(281)
Propane	−187.65	(121)	−42.06	(121)
Butane	−138.29	(15)	−0.50	(15)
Propene	−189.9	(147)	−47.8	(51)
	−184.9	(106)	−47.0	(147)
			−47.5	(262)
			−47.64	(7)
			−47.76	(128)
			−47.8	(36, 38)
	−185.24	(180)	−47.74	(180)
Acetylene	−81.8	(147)	−84.0	(37, 38)
Methyl chloride	−97.72	(157)	−24.22	(157)
Methyl bromide	−93.66	(58)	3.56	(58)
Cyclopropane	−127.56	(189)	−32.77	(7)
			−32.80	(189)
	−12.7	(261)	−34.2	(261)
Ethylacetylene	−122.5	(166)	8.6	(166)
Methylacetylene	−101.5	(166)	−23.3	(166)
			−23.1	(88)
Methylamine	−93.46	(17)	−6.32	(17)
Dimethylamine	−92.19	(10)	6.88	(10)
Trimethylamine	−117.08	(16)	2.87	(16)
Tetramethylmethane	−16.63	(14)	9.45	(14)
Isobutane	−159.42	(13)	−11.72	(13)
1-Butene	−185.34	(11)	−6.25	(11)
2-Butene (*trans* and *cis*)	−127	(40)	1.0	(40)

TABLE 1—*Continued*

COMPOUND	MELTING OR TRIPLE POINT	REFERENCE	NORMAL BOILING POINT	REFERENCE
	°C.		°C.	
2-Butene (*trans*)	−105.55	(84)	0.88	(85)
2-Butene (*cis*)	−139.3*	(128)	3.73	(128)
	−136.3	(254)	3.53	(130)
	−138.90	(204)	3.72	(204)
Isobutene	−146.8	(40)	−6.6	(40)
	−140.7	(128)	−6.97	(128)
	−140.7	(254)	−7.12	(130)
	−139	(248)		
Allene			−35.0	(143)
Fluoroform	−160	(191)	−82.2	(89)
			−84.4	(191)
Cyanogen	−27.90	(175)	−21.17	(175)
Dimethyl ether	−138.0	(145)	−24.9	(145)
	−141.50	(122)	−24.82	(122)
Ethylene oxide	−111.3	(145)	10.73	(145)
Carbon tetrafluoride	−183.6	(156)	−128.00	(156)
	−183.69	(64)		

* Impurity 0.1 per cent as determined by Todd and Parks.

tane thermometer and placed in a cold bath of acetone and petroleum ether which was allowed to warm up at about 1° per minute until melting occurred (the conventional method of the organic chemist). This method, hereafter referred to as method II, yields results accurate to 1° or so but with modifications can be made more accurate.

Later (248, 250) a platinum resistance thermometer replaced the pentane thermometer in Timmermans' more accurate measurements by method I. Curves were plotted of the temperatures of the well-stirred mixture during slow cooling, and the melting point was obtained from the temperature of the flat portion. This procedure (method I) with platinum resistance thermometer or thermocouple has been used by other investigators (98, 149, 185).

The rate of cooling can be controlled by placing the sample in a Dewar vessel and varying the vacuum between the walls (149, 213). Roper (185), while obtaining cooling curves by method I, takes particular pains to have the temperature of the outer cooling bath falling at a constant known rate. He used a cryostat of type *c* (225) for this purpose. Thus the rate of cooling of the sample was practically equal to that of the bath until the freezing point was reached, and the cooling curves were more easily interpreted. Such a procedure is to be recommended. It has been used previously by others with somewhat less precision (4, 181, 238).

Taylor and Rossini (237) have developed a method for the theoretical analysis of certain time-temperature freezing and melting curves as applied to hydrocarbons. Their method is a further refinement of the method used by Mair, Glasgow, and Rossini (150), who showed that in dealing with time-temperature freezing and melting curves obtained on hydrocarbons, when significant undercooling occurs on freezing, the observation can be analyzed to yield, in proper relation to the subsequent equilibrium part of the curve, the time at which crystallization would have begun in the absence of undercooling. Mair, Glasgow, and Rossini employed a visual extrapolation of the equilibrium curve to zero time, while Taylor and Rossini developed a method, which may be used analytically or graphically, for extrapolating the equilibrium part of a time-temperature freezing or melting curve to give the freezing or melting point of the substance under study.

They also describe a method for deducing, within certain wide limits, from the same observations on the substance under study the freezing point for zero impurity which, together with the freezing point of the sample and its molar heat of fusion, enables one to calculate the amount of liquid-soluble, solid-insoluble impurity. By proper calibration of the instrument, it is possible to obtain heats of fusion directly.

Skau (210) has developed an apparatus in which only 0.5 to 0.7 g. of material is required to obtain cooling curves. In principle his method is the same as that of Roper.

Method II has been used by Maass and his collaborators (40, 147). The accuracy was improved by using a larger bulb of the substance and holding the temperature at the melting point for several minutes.

The most accurate method for measuring melting points is to carry out the determination in a vacuum-jacketed calorimeter of one of the types discussed in connection with the paragraphs on specific heats which follow. This will be referred to as method III. If there are any impurities, as the melting point of the sample is approached a small fraction of the solid melts to a solution which contains the impurities (premelting). The heat necessary for this melting causes an obvious abnormal rise in the specific heat. Finally, at the freezing point all the heat put into the calorimeter is absorbed in fusion, and for a highly purified compound only very slight temperature increases (a few thousandths of a degree) result from the input of sufficient energy to melt the remaining 90 per cent of the material. Thus the melting point is easily ascertained. The more impurity is present, the lower is the temperature at which obvious premelting is encountered. From the fraction melted at any temperature below the freezing point, the percentage of impurity in the sample can readily be calculated, assuming the laws of perfect solution (109). The fraction melted is calculated from the energy input above that due to the specific heat, using an approximate heat of fusion. By freezing point is meant the equilibrium temperature in the calorimeter when the amount of crystals is negligibly small. This value can then be corrected for the lowering caused by the impurity to obtain the melting point of the pure material.

Aston, Fink, Tooke, and Cines (12) describe a melting-point calorimeter whose basic design is similar to that of a precision adiabatic calorimeter, described in Section IX, in which some accuracy is sacrificed for speed. The sample is poured into the calorimeter, thereby greatly facilitating filling, and the operation of the calorimeter has been simplified to enable operation by one person.

A further advantage of the calorimetric determinations of purity over the freezing-point determinations of purity is that it is possible to detect solid solution simultaneously with the purity determination by comparing the impurity calculated from premelting heat capacities with that calculated from the fusion temperatures. This method has been described by Aston, Cines, and Fink (8).

A simple heat-conductivity calorimeter for melting-point determinations been described by Fischl (70). This method is advantageous as compared to method I in cases where excessive supercooling occurs, as has been noticed in high-molecular-weight hydrocarbons.

The calorimeter consists of a copper ampoule, with a thermocouple attached, in which the sample under study is placed, suspended from a heavy copper shield. The shield is kept at about 2–3° above that of the ampoule, and time–temperature readings of the shield and ampoule are recorded until the entire sample is molten. The results obtained with this apparatus are less precise than those obtained with the electrically heated adiabatic melting-point calorimeter.

It is important to realize that measurements can be taken, by method III, when almost all of the material is melted, whereas other methods require a mush of crystals and consequent concentration of impurities by freezing.

In the course of the work of the Bureau International (247) on the physical properties of organic compounds, Timmermans has measured the freezing points of a large number of organic compounds by method I with an accuracy depending on the purity of the organic compounds.

A number of investigations have been made to determine the freezing points or triple points of certain pure organic compounds with sufficient accuracy (about 0.02°) so that they could serve as fixed points on the temperature scale. The freezing points were measured against a resistance thermometer or thermocouple that had been compared directly with a gas thermometer. For such an investigation, Keyes, Townshend, and Young at the Massachusetts Institute of Technology (124) placed the organic liquid in the inner Dewar of a small cryostat of type *c* from which the heater was omitted. Stirring was accomplished by air. The cooling was effected by liquid air in the outer Dewar, and its rate controlled by adjusting the vacuum between the walls of the inner Dewar. A thermocouple previously calibrated against a nitrogen thermometer was used to read the temperature of the solid–liquid equilibrium mixture. The results are recorded in table 2 (column 4).

In a similar investigation by Timmermans, van der Horst, and Kamerlingh Onnes (251), a well-stirred tube of the liquid was cooled by a current of cold air whose temperature was adjusted to give the required rate of cooling. A platinum resistance thermometer which had been previously compared with a helium thermometer was used to read the equilibrium temperature of the well-stirred solid–liquid mush at the freezing point. The values obtained have been revised by Timmermans (249). The revised results are summarized in table 2 (column 2).

Similarly, the melting points of several organic compounds have been determined by Henning at the Reichsanstalt by method I, using a platinum resistance thermometer which had been calibrated against a helium thermometer (90). The fixed points thus obtained appear in column 3 of table 2.

Timmermans (249) has discussed these three sets of fixed points and concludes that the differences are due to impurities in the Reichsanstalt and the M.I.T. compounds.

TABLE 2

Melting points of organic compounds

COMPOUNDS	LEIDEN: TIMMERMANS, VAN DER HORST, AND KAMERLINGH ONNES (249,251)	REICHSANSTALT: HENNING (90)	MASSACHUSETTS INSTITUTE OF TECHNOLOGY: KEYES, TOWNSHEND, AND YOUNG (124)	*CALIFORNIA (120) (TRIPLE POINT), **PENNSYLVANIA STATE (157) (TRIPLE POINT); ***INTERNATIONAL (185) (ROPER)
	°C.	°C.	°C.	°C.
Carbon tetrachloride...	−22.85		−22.87	
Chloroform..........	−63.7	−63.6	−64.19	
Chlorobenzene.........	−45.35	−45.5	−45.58	
Ethyl acetate.........	−83.6			
Toluene...............	−95.0		−95.70	
Carbon bisulfide........	−111.8	−112.0	−112.97	
Diethyl ether:				
Stable..............	−116.3		−115.9	
Unstable...............	−123.3	−123.6	−123.40	
Methyl chloride............			−98.39	−97.72**
Methyl alcohol.............			−98.54	−97.88* −97.68***

In column 5 of table 2 are recorded the melting points of any of these substances which have been determined against the temperature scale of other laboratories.

Transition points can be determined in exactly the same way as melting points. In this case the superiority of method III is quite evident.

Table 1 lists melting points for some organic substances which boil below room temperature.

Phase (freezing-point) diagrams have been constructed for binary liquids at low temperatures. Mixtures of certain chloro compounds have been studied by Timmermans and Vesselovsky (252). 1,2-Dichloroethane and 1,1,2,2-tetrachloroethane form an equimolecular compound melting at −32°C. The melting point for the compound of the corresponding bromo compounds is −8.25°C. (non-congruent). The dichloroethane forms an equimolecular compound with the tetrabromoethane (non-congruent m.p. −28.5°C.); so also does the dibromoethane with the tetrachloroethane (non-congruent m.p. −35°C.).

Huelting and Smyth (105) find no compound formation between 1,2-dichloroethane and benzene, but the former forms a compound with diethyl ether (m.p. −103°C.). A freezing-point study of a number of pure hydrocarbons and their binary mixtures (213) reveals that as a rule solutions of the hydrocarbons behave ideally, but *n*-octane–*n*-nonane and 2,2,3-trimethylbutane–2,2,3,3-tetramethylbutane are systems which yield mixed crystals.

VII. DENSITY

The measurement of densities of liquids below room temperature has been made for four main reasons: (*1*) because physical properties of low members of homologous series are of particular interest and these are liquids only at low temperatures; (*2*) to verify the law of rectilinear diameters, which states that the mean of the densities of a liquid and its saturated vapor lie on a straight line passing through the critical temperature; (*3*) to obtain density for the purpose of calculating molecular refractions and polarizations (221); and (*4*) to be used in calculating thermodynamic properties. The results can be used to verify the results of the law of corresponding states,—that the ratio of the densities of two liquids at the same corresponding temperature is a constant (147, 172). For one reason or another a large number of simple organic compounds have been investigated.

The pycnometers (or dilatometers) employed can be either a bulb with a long graduated capillary (147) or the U-shaped pycnometer (123) commonly used at ordinary temperatures. If the former is used, a single weight of liquid serves for several temperatures, as the increasing volume is read by the position of the meniscus in the capillary. Low-boiling liquids such as dimethyl ether, whose vapor pressure is less than 10 atm. at room temperature, can be weighed directly in the pycnometer (147) or weighed in glass bulbs after distillation from the pycnometer (172). The weight of lower boiling liquids must be measured by taking a known volume of gas and calculating the weight from the density of the gas (123, 179). In any case, for temperatures where the vapor pressure is appreciable the weight of vapor above the liquid must be subtracted from the total weight. Constant temperatures are best obtained by cryostats of types *c* or *d*.

The liquid densities of methane have been determined by Keyes, Taylor, and Smith (123) as part of an investigation on the thermodynamic properties of methane made in connection with the recovery of helium from natural gas. Porter (179) has studied the densities of liquid ethane at low temperatures as part of the program on hydrocarbon research at the U. S. Bureau of Mines. The densities of liquid ethylene at low temperatures have been measured by Mathias, Crommelin, and Watts (152, 153), who showed that this gas obeys the law of rectilinear diameters only approximately.

Maass and his coworkers have made measurements on the density of the lower hydrocarbons in most cases down to near their melting point. Their work has included ethane, propane, ethylene, acetylene, propylene (147), isobutylene (41), butane and isobutane (40), methyl- and ethyl-acetylenes (166), dimethyl- and *n*-propylacetylenes (167). The work was done as part of a study of the general physical properties of these lower hydrocarbons.

The densities of liquid and gaseous propane, butane, and isobutane have been determined by Dana, Jenkins, Burdick, and Timm as part of an investigation of their thermodynamic properties (51). Timmermans has determined liquid densities on pentane and isopentane (244).

Certain simple fluorinated hydrocarbons have recently been prepared in a relatively pure state by Ruff and his coworkers, who have reported liquid densities at low temperatures on fluoroform (191) and carbon tetrafluoride (192), tetrafluoromethane and hexafluoroethane (190), and chlorotrifluoromethane, dichlorodifluoromethane, and trichlorofluoromethane (193).

Early work by Timmermans on liquid densities down to near the melting point was carried out to test the law of rectilinear diameters in the region of low gas densities. The compounds investigated were methyl and ethyl alcohols, ether, acetone, isobutyric acid, ethyl acetate, acetonitrile, ethyl bromide, chloroform, isopentane, toluene, chlorobenzene, and pyridine (241), and ethyl acetate (242). Acetone has more recently been studied down to −90°C. (5, 69).

As part of a study of the thermodynamic properties of diethyl ether, Taylor and Smith (236) have made a thorough study of the densities of the liquid at low temperatures. Dimethyl ether and ethylene oxide have been investigated as part of a study of their physical properties (145).

Smyth and his coworkers have made studies of liquid densities at low temperatures for the purpose of calculating values of the polarization from the dielectric-constant measurements (57, 214, 221, 222, 223). Morgan and Lowry have carried out similar work on other compounds (168). The compounds studied in both cases are listed in table 3 in the section on dielectric constants.

As part of a general study on physical properties, Tonomura (256) has measured the liquid densities down to −100°C. of isopropyl, *n*-butyl, and allyl alcohols, toluene, and methyl ethyl ketone. Mitsukuri and Kitano have studied propyl and isobutyl alcohols (161).

Schaufelberger (200) has determined the densities of low-boiling liquids by condensing them in an unsilvered Dewar. The density is then read by a hydrometer.

An important investigation has been carried out by Heuse (93) on the densities of certain solid organic compounds at liquid-hydrogen temperatures. The purpose of the investigation was a comparison of the molecular volumes at the absolute zero with those calculated from the volumes of the constituent atoms by Kopp's Law. The volume of the solid hydrocarbon was measured by ascertaining the free volume in the container. This was done by expanding helium from the container into a known volume. From the initial and final pressures the original volume occupied by the gas could be calculated. The aromatic hydrocarbons (benzene, toluene, *m*-xylene, ethylbenzene, propylbenzene, mesitylene, and naphthalene) had molecular volumes within experimental error of those calculated using Kopp's Law. So did ethylene. On the other hand, the normal saturated hydrocarbons from ethane to nonane, isopentane, and cyclohexane had molecular volumes lower than those calculated by Kopp's Law. For methane the reverse was true. It does not seem that data on molecular volumes at low temperatures possess any marked advantage from the standpoint of the use of additivity relations in determining structure.

The change of molecular volume with temperature in the neighborhood of the transition point where rotation sets in has been studied for solid *d*-camphor and camphor (278).

VIII. DIELECTRIC CONSTANT

As is well known, the average electric moment of a molecule can be calculated from dielectric-constant measurements of solutions in a non-polar solvent (54). Briefly, the polarization (P) is first calculated from the dielectric constant (ϵ) using the relation

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2}\,\frac{M_1N_1 + M_2N_2}{\rho} \tag{2}$$

where ρ is the density and M_1 and M_2 are, respectively, the molecular weights of the non-polar solvent and of the solute whose electric moment is to be found. The respective mole fractions are N_1 and N_2.

The polarization, P_2, of the solute can be calculated from the relation

$$P_{12} = P_1N_1 + P_2N_2 \tag{3}$$

if P_1, the polarization of the pure solvent, is known. Such measurements yield values of P_2 dependent on the concentration. From a plot of P_2 against N_2 the value of P_2 at zero concentration can be obtained; it is characteristic of the free polar molecule if there is no interaction with the solvent. This limiting value of P_2 will be denoted by P_0 and can be considered as being due to (*a*) P_E, the electronic polarization due to electronic shifts, (*b*) P_A, the atomic polarization due to the shift of atoms or radicals, and (*c*) P_M, which is due to the orientation of molecules of electric moment μ in the field. So that

$$P_0 = P_E + P_A + P_M \tag{4}$$

if P_0 be plotted against $1/T$ from data over a range of temperatures, a straight line is obtained.

$$P_0 = a + b/T \tag{5}$$

where $a = P_E + P_A$ and $b = 4\pi N\mu^2/9k = P_MT$. ($N$ is the Avogadro number and k is the Boltzmann gas constant.) This same equation obviously applies to the polarization of a pure gas at zero pressure.

For most non-polar solvents (e.g., hexane, benzene, carbon tetrachloride) it is necessary, because of low boiling points, to go to low temperatures (i.e., to just above the freezing point) to obtain a suitable range of values for accurate calculation of b (and hence of μ) from the slope of the P_0 *vs.* $1/T$ plot.

It is well known that to obtain ϵ one obtains the ratio of the capacity of a condenser, filled with the solution, to that of air.

The work of Smyth and Morgan (221), who obtained the electric moments of ethyl bromide, chloroform, and chlorobenzene from such measurements in hexane, is illustrative of the methods used. They made measurements from −90°C. to +60°C. and employed a cell consisting of three concentric platinum cylinders encased between two glass cylinders sealed together at the top and bottom so as to hold the liquid between them. Constant temperatures in the low range were obtained by use of a cryostat of type *d*. Temperatures were measured by using a platinum resistance thermometer placed inside the hollow ring of the cell. The results of such measurements by several investigators are given in table 3.

The moment of ethyl iodide was obtained from measurements in heptane solution down to −100°C. Ethyl alcohol was studied down to −110°C. in hexane and heptane; *n*-butyl alcohol in heptane (down to −90°C.); *n*-octyl alcohol in heptane (only to −30°C.) (223). Butyl chloride, bromide, and iodide as well as heptyl bromide and ethylene dibromide have been measured in heptane; diiodomethane, bromoform, and iodoform were studied in benzene (222), some down to −90°C. In order to study the change of electric moment with temperature ethyl acetate, ethylene dichloride, and ethylene chlorobromide were measured in heptane down to low temperatures (214).

A thorough study of the dielectric constants and densities of all the normal saturated hydrocarbons from pentane to dodecane at temperatures covering the entire liquid range has been made (57). The polarization did not change with temperature, indicating a vanishingly small electric moment. The investigations of dielectric constants of gaseous methane extended down to −154°C. (184) and of gaseous ethane and propane down to −80°C. (224, 277) and showed no moment. Measurements of dielectric constant on the gases down to −80°C. also showed ethylene, acetylene (224, 276), and carbon tetrafluoride (224, 277) to have no moment. On the other hand, similar measurements have shown propene (276) to have a small moment (0.37×10^{-18}). While the range of investigation did not extend below 0°C., temperature coefficients of the dielectric constants of butene, 2-methylpropene ("isobutene"), and methylacetylene show small moments (224, 277) in the order 0.30×10^{-18}, 0.49×10^{-18}, 0.72×10^{-18}. It is curious that allene also shows a moment.

From table 3 it is noticed that the moment of ethylene dichloride and of ethylene chlorobromide changes with temperature. This has been interpreted (158, 214) to mean that the repulsive effect of the dipoles favors the *trans* position. If the potential associated with the effect is of the order of 2000 cal. and causes most of the molecules to oscillate about the *trans* position in a way that may be treated as a classical vibration (214), such an assumption explains the temperature effect.

Just as the dielectric constant decreases with rise in temperature it will decrease with frequency if the medium is sufficiently viscous. In this case, the time of the relaxation of the system is too long to allow the dipole orientation to follow the alternation in current. The higher the viscosity the lower the frequency at which this change with frequency (anomalous dispersion) can be observed.

By working at low temperatures (down to −90°C.) the change with frequency

TABLE 3

Electric moments obtained from low-temperature dielectric-constant measurements in solution

COMPOUND	SOLVENT	TEMPERATURE RANGE	MOMENT $\mu \times 10^{18}$	REFERENCE
		°C.		
n-Hexane	None	−90 to +60	0	(221)
Ethyl bromide	*n*-Hexane	−90 to +60	1.86	(221)
Chloroform	*n*-Hexane	−90 to +60	1.05	(221)
Chlorobenzene	*n*-Hexane	−80 to +60	1.52	(221)
Ethyl iodide	*n*-Heptane	−100 to +70	1.66	(223)
Ethyl alcohol	*n*-Hexane	−90 to +60	Association	(223)
Ethyl alcohol	*n*-Heptane	−110 to +60	Association	(223)
n-Butyl alcohol	*n*-Heptane	−90 to +90	Association	(223)
n-Octyl alcohol	*n*-Heptane	−30 to +60	Association	(223)
Ethylene dichloride	a. *n*-Heptane	−90 to +70	1.16 at −50°C.	(100, 214)
	b. *n*-Amylene		1.41 at +30°C.	(164)
Ethylene dichloride	*n*-Hexane	−71 to +40.9	2.4 at $1/T = 0$	(101, 158)
Ethylene chlorobromide	a. *n*-Heptane	−50 to +90	0.92 at −50°C.	(214)
	b. *n*-Hexane		1.19 at +30°C.	(214)
Ethyl acetate	*n*-Heptane	−90 to +70	1.57 at all °T.	(214)
Ethylene dibromide	a. *n*-Heptane b. *n*-Hexane c. Benzene	−40 to +90	0.57 at −50°C. 0.92 at +50°C.	(101, 218)
Trimethylene bromide	*n*-Heptane	−30 to +70	2.19 at +50°C.	(218)
Pentamethylene bromide	*n*-Heptane	−40 to +90	2.47 at +40°C.	(218)
Ethyl alcohol	Diethyl ether	−60 to +25	1.79	(99)
Ethylene glycol	Diethyl ether	−60 to +20	1.2 at −60° 2.4 at +20°	(99)
Acetic acid	Diethyl ether	−60 to +25	0.72 at −60° 1.23 at +25°	(99)
n-Butyl chloride	Heptane	−90 to +70	1.88	(222)
n-Butyl iodide	Heptane	−80 to +80	1.59	(222)
n-Butyl bromide	Heptane	−90 to +90	1.81	(222)
n-Heptyl bromide	Heptane	−70 to +90	1.83	(222)
Pentane	None	−90 to +30	0.0	(57)
Hexane	None	−90 to +50	0.0	(57)
Heptane	None	−90 to +90	0.0	(57)
Octane	None	−50 to +50	0.0	(57)
Nonane	None	−50 to +50	0.0	(57)
Decane	None	−30 to +170	0.0	(57)
Undecane	None	−10 to +190	0.0	(57)
Dodecane	None	−10 to +210	0.0	(57)
Methyl chloride*	Carbon tetrachloride	−46 to +18	1.56	(168)
Methyl chloride*	Hexane	−106.2 to +42.2	1.65	(168)
Dichloromethane*	Carbon tetrachloride	−89 to +40.5	1.48	(168)
Methyl bromide*	Hexane	−103.4 to +37	1.45	(168)
Methyl iodide*	Hexane	−87 to +33.7	1.35	(168)

* Investigation also carried out on the solid.

has been observed at 1 kilocycle for a series of glycols, whereas at ordinary temperatures there is no change with frequency until the frequency is greater than 100 kilocycles (280).

The dielectric constants of simple crystalline organic compounds which melt considerably below room temperatures are of considerable interest, because in certain cases they yield evidence concerning the rotation of molecules in crystals.

If the molecule is held rigidly in the crystal, the polarization is due only to electronic and atomic displacements; that is,

$$P = P_E + P_A \tag{6}$$

As a result the dielectric constant is low. Furthermore, the apparent dielectric constant measured (with a constant weight of crystals between the plates of the condenser) is almost independent of temperature and frequency. A very slight temperature and frequency dependence is due to the increased opportunity for atomic polarization as the structure becomes slightly more open with rising temperature. There have been very few substances found for which the dielectric constant of the solid has been found to behave otherwise. 1-Octanol (219) is typical of the usual solid with a dielectric constant of 2.32 at 87.3°K., 2.34 at 179.1°K., and 2.77 at 251.3°K. These values were determined at a frequency of 50 kilocycles. Dielectric-constant measurements have been made in the liquid and solid states for oxygen, chlorine, and hydrogen chloride (112). The last of these does not follow equation 6 since, apparently, there is a rotation in the crystal below the melting point.

The dielectric constants of solid hydrogen chloride, hydrogen bromide, and hydrogen iodide, which have been studied down to −190°C. (216), below the melting point increase rapidly as the temperature decreases. The same can be said of the polarizations. This behavior is due to the rotation of the molecules in the solid state. All three molecules exhibit transitions. Hydrogen chloride exhibits one such transition. Between this transition and the melting point the polarization obeys equation 5, indicating dipole orientation in the solid state, but below this transition the dielectric constant drops to such a low value that there is evidently little possibility of dipole orientation. The behavior of the other hydrogen halides is similar, but for these there is more than one transition and the behavior of the dielectric constant and polarization between them is complicated. These studies have been extended to hydrogen cyanide, hydrogen selenide, and arsine (220). In the last case, measurements were made down to liquid-hydrogen temperatures (20°K.). Hydrogen selenide rotates freely in the solid state down to −190°C., but hydrogen cyanide does not rotate at all. Arsine rotates freely down to 32.1°K., where a transition sets in.

Methyl alcohol (217, 219) in the solid state exhibits an abnormally high dielectric constant which increases with temperature. Its value for 5 kilocycles is 3.28 at 108.4°K. and rises to 4.66 at 159.9°K., where there is a transition to a form whose dielectric constant is 5.65 at the same temperature and 9.00 at 169°K. (6.4° below the melting point). These results point to freedom of the methyl alcohol to turn in the crystal with the field above the transition temperature. They point against actual rotation in the crystal in the absence of the field, because such a situation would give rise to a dielectric constant rising as the temperature fell, as is the case for the solid hydrogen halides (216). Moreover, as other alcohols (219) behave like 1-octanol, it must be the whole molecule which can orient itself with the field and not the OH group alone. Dimethyl sulfate (215) in the solid state at 60 kilocycles shows abnormally high values of the dielectric constant, which decrease with rising temperatures as for the hydrogen halides. This is to be attributed to rotation of the methoxyl group for several molecules in the crystal in the absence of the field. Information on other methoxyl compounds would be interesting, although solid anisole and hydroquinone dimethyl ether do not show this behavior (111).

In view of the result with methyl alcohol it is surprising that methylamine (155) shows the dielectric-constant values of the ordinary solid. Diethyl ether, acetone, benzophenone, and succinic acid (155), the methyl halides, methylene chloride, and chloroform (168) also show no evidence of orientation or rotation in the solid. The dielectric-constant measurements, however, show nothing about the rotation of the methyl group about its axis, as this group has no electric moment and therefore does not contribute to the dielectric constant.

Measurements of the dielectric constant of ethylene cyanide have been made from −190° to 78.2°C. (279). The polarization suffers no sharp change at the freezing point (54.2°C.). The discontinuity in the polarization at about −40°C. accompanies a transition, and it is probably only below this that rotation about any axis is restricted in the solid. Below this point, there is probably no rotation in the solid. Similar measurements on ethylene dichloride, ethylene dibromide, ethylene thiocyanate, and ethylenediamine show that there is no dipole rotation in these solids (279).

Isobutyl chloride, isoamyl chloride, tertiary amyl chloride, and 1,2-dichloro-2-methylpropane do not rotate in the solid state (263). Low-temperature dielectric-constant measurements on *d*-camphor, *dl*-camphor, and bornyl chloride show dipole rotation above transition points which occur at about −40°, −60°, and −110°C., respectively (284). Studies of the change of heat capacity and molecular volume at the transition and of the entropy of fusion confirm this conclusion (278).

A thorough study of the effect of pressure and temperature on the dielectric constants of hydrogen, deuterium, helium, oxygen, air, and carbon monoxide has been made by van Itterbeek and Spaepen (266). They made measurements between 20°K. and room temperature and found the dipole moment of carbon monoxide to be 0.11×10^{-18}. The same authors have made measurements on liquid deuterium (265). Measurements on liquid and solid hydrogen (82) and on nitrogen (81) have been made by Guillien and on helium I and II by Wolfke (282). Conner and Smyth (44) have used dielectric-constant measurements to study the solid–liquid equilibrium diagram of the system carbon tetrachloride–*tert*-butyl chloride.

IX. HEAT CAPACITY, HEAT OF FUSION, HEAT OF TRANSITION, AND HEAT OF VAPORIZATION

The object of most low-temperature heat-capacity determinations is either the determination of the entropy or the procurement of data for comparison with results calculated on the basis of the theory of the solid or gaseous state.

To obtain the entropy the following equation is used:

$$S - S_0 = \int_0^{12} C_p \,\mathrm{d} \ln T + \int_{12}^{T_t} C_p \,\mathrm{d} \ln T + \frac{\Delta H_t}{T_t} + \int_{T_t}^{T_m} C_p \,\mathrm{d} \ln T + \frac{\Delta H_m}{T} + \int_{T_m}^{T_v} C_p \,\mathrm{d} \ln T + \frac{\Delta H_v}{T} + \int_{T_v}^{T} C_p \,\mathrm{d} \ln T$$

where the first integral represents an extrapolation below 12°K., and T_t, T_m, and T_v are temperatures of transition, melting, and vaporization, while ΔH_t, ΔH_m, and ΔH_v are the corresponding molal heat effects associated with these changes. C_p is the molal heat capacity of the phase. Temperatures down to 10°K. are obtained by pumping on solid hydrogen.

Most of the heat-capacity determinations at low temperatures have been performed using the technique originally devised by Nernst (170) and Eucken (62). In the earliest measurements of specific heats of metals at low temperatures, the substance itself acted as the calorimeter. A block of the material was suspended inside of a jacket of very large heat capacity which in turn was placed in a Dewar flask containing the refrigerant. The jacket was evacuated to provide thermal isolation, the calorimeter was heated by supplying a known amount of electrical energy, and the rise in temperature was observed by a thermocouple or resistance thermometer. Corrections had to be applied for radiation and other heat leaks. At temperatures below that of the boiling point of liquid air these corrections were quite small, but at higher temperatures they were so large as to make the results quite inaccurate.

This difficulty has been corrected somewhat by Nernst and Schwers (171), Gibson and coworkers (77, 78), Giauque and coworkers (74, 75, 76), and others (1, 3, 14, 85, 134, 135, 160, 173) by using shields of various types which keep the temperatures of the surroundings very near to that of the calorimeter. Although this method is a vast improvement over the original technique, the necessity of correcting for thermal leakage (usually of the order of 0.05 to 1.0 per cent) still remained, which as a rule decreased the accuracy of the final results. Obviously, the ideal condition is to keep the temperature of the shield at all times exactly equal to that of the calorimeter. This situation is approximated very closely in the so-called adiabatic calorimeter. The calculation of results is thus much simpler, as there are no corrections to be made for heat leaks, radiation, etc.

The first adiabatic calorimeter was employed by Lange (132) and later further developed by Southard and Andrews (226), Southard and Brickwedde (227), Aston and Eidinoff (9), Yost *et al.* (285), Ruehrwein and Huffman (188), and Scott and Brickwedde (204, 205).

A less precise apparatus (1–3 per cent) for measuring heat capacity at low temperatures has been developed by Andrews and coworkers (2, 87, 212, 232, 286). This is called the calibrated heat-conductivity calorimeter. The calorimeter is heated by conduction and radiation from a surrounding jacket by means of a constant thermal head. The rate of temperature rise of the calorimeter under these conditions is compared with the rate of rise obtained under the same conditions when the calorimeter contains a standard substance of known heat capacity.

The most accurate heats of fusion and transition are obtained in the adiabatic calorimeter discussed above, which is also used to measure heat capacities. The heat necessary to raise the temperature of a known amount of substance from slightly below its melting point to slightly above its melting point is measured, and appropriate corrections are applied as described in the references mentioned. Heats of fusion and transition may also be obtained in the calibrated heat-conductivity calorimeter.

Heats of vaporization of pure substances may be determined in either the Nernst type or the adiabatic type of calorimeter. The only important additions are a filling tube through which the material is vaporized and a means of measuring the amount of liquid vaporized. With low-boiling substances, the vaporized material may be collected in the gas state and its volume measured, or it can sometimes be absorbed chemically. The vapor may be condensed at a low temperature, or at a regulated temperature slightly below that of the calorimeter.

Heats of vaporization of binary mixtures present many difficulties. According to the conditions under which the mixture is evaporated, different values may be obtained. In a static system, the liquid and vapor composition will vary during the experiment and the final results obtained are for averaged vapor and liquid composition. Using a dynamic method, Dana (50) succeeded in measuring heats of vaporization at constant pressure and composition for mixtures of oxygen and nitrogen at atmospheric pressure. With an electrical heating coil, liquid mixtures of oxygen and nitrogen were evaporated from an insulated glass vessel, liquid of constant composition being continuously introduced into the calorimeter. In the stationary state, the vapor leaving the apparatus must have the same composition as the liquid introduced. At the same time, the liquid in the calorimeter will be enriched with oxygen, so as to be in equilibrium with the escaping vapor. But this liquid does not enter into the process. From the quantity of heat introduced and the amount of vapor leaving the apparatus in a given time, the heat of vaporization is obtained for the composition of the escaping vapor.

For the determination of heat capacities of gases at low temperatures the conventional flow method is only applicable in a limited number of cases, since the pressure at which most substances condense is considerably below 1 atm.

The most widely used method is the "hot wire" method of Eucken and Weigert, which is essentially a thermal conductivity method (64). This method can be used at pressures as low as 10^{-3} mm. of mercury. The apparatus can be maintained at low temperatures in cryostats of types *a*, *b*, *c*, and *d*. The method has been used to study the heat capacity of ethane down to 94°K. (107, 125, 127).

X. PHASE EQUILIBRIA

A. Liquid–vapor equilibrium

An excellent review of the methods of obtaining data on liquid–vapor equilibrium is presented by Ruhemann (195) in his book entitled *The Separation of Gases*; certain sections below are quoted almost directly from his book. Only the low-temperature techniques are presented.

Ruhemann has divided the methods for obtaining liquid–vapor equilibrium roughly into four groups: (*1*) dew- and boiling-point method; (*2*) static method; (*3*) flow method; (*4*) circulation method. These methods will be discussed independently.

In the dew- and boiling-point method a gas of known composition is introduced into the equilibrium vessel at constant temperature, and the pressures at which condensation starts and is completed are observed. This method has been used by Holst and Hamburger (103) on argon-nitrogen mixtures, by Bourbo and Ischkin (32) on argon–oxygen mixtures, and by Steckel (229) on nitrogen–carbon monoxide mixtures; Sage and Lacey (197, 198) have used it for light hydrocarbon mixtures. The advantage of this method is that the phases need not be analyzed as mixtures may be composed arbitrarily, but great care must be used if accurate results are to be obtained.

In the static method a mixture is confined in the equilibrium vessel at constant temperature and pressure and the compositions of the liquid and vapor phases in equilibrium are determined. Baly (20) first used the static method to determine the equilibrium of oxygen–nitrogen mixtures. The static method was also used by Verschoyle (267) for nitrogen–hydrogen, carbon monoxide–hydrogen, and nitrogen–carbon monoxide–hydrogen, by Freeth and Verschoyle (72) for hydrogen–methane mixtures, by Fedoritenko and Ruhemann (67) for mixtures of nitrogen and helium, and by Torocheshnikov and Ershova (260) for argon–oxygen–nitrogen mixtures. The main disadvantage of this method is that equilibrium may be destroyed when samples are drawn for analysis. Thus the method is more reliable at high pressure than at low pressure.

In the flow method, the gas is passed slowly and continuously at constant pressure through an apparatus which is constructed to ensure good thermal contact. The gaseous phase flows into a gasometer, and the liquid phase collects in the equilibrium vessel. The gas and liquid may be analyzed either during the measurement or at the end of the measurement. This method has been used by Steckel and Zinn (230) for hydrogen–nitrogen–methane mixtures, by Ruhemann and Zinn (196) with hydrogen–nitrogen–carbon monoxide mixtures, by Fedoritenko and Ruhemann (67) for nitrogen–helium mixtures, by Ruhemann (194) for methane–ethane mixtures, and by Guter, Newitt, and Ruhemann (83) for methane–ethylene mixtures. The disadvantage of this method is that the equilibrium vessel may become too full of liquid because of too rapid condensation, thereby upsetting the equilibrium.

In the circulation method, the gas is circulated through the liquid in the equilibrium vessel at constant temperature and pressure until equilibrium is established. This is ascertained by continuous analysis of the liquid and vapor states until constant analyses are obtained. This method was developed by Dodge and Dunbar (56) for studies of mixtures of oxygen and nitrogen. It has also been used by Torocheshnikov (259) for mixtures of carbon monoxide and nitrogen. This method is probably the most accurate and reliable of all existing methods but demands a rather elaborate and complicated equipment. Cryostats of types *a*, *b*, *c*, and *d* can be used to maintain the necessary temperatures.

B. Solid–liquid equilibrium

The methods of obtaining solid–liquid equilibrium have been discussed in the section dealing with melting points.

XI. ADSORPTION OF GASES ON SOLIDS

An advanced discussion of the theory and methods of physical adsorption has been presented by Brunauer (33) in his book *Physical Adsorption.* For methods of desorption and the proper preparation of the surface of the adsorbent, the reader is referred to this treatise.

A. Determination of adsorption isotherms

The determination of the amount of gas adsorbed on a solid may be determined by the following method: The adsorbent is separated from the measuring apparatus during evacuation by a stopcock and immersed during measurements in a proper thermostat. Prior to adsorption the volume and pressure of the gas are measured, and then the stopcock is opened to the evacuated adsorbent. After adsorption, the volume and pressure of the gas are again measured. Part of the gas is adsorbed and part fills the dead space in the adsorbent. To determine this dead space, a non-adsorbing gas such as helium usually is employed in the same apparatus. Relatively simple apparatus for these determinations has been described by Homfray (104), Titoff (253), Richardson (183), and Pease (174).

A somewhat more complicated apparatus has been described by Coolidge (45) for the adsorption of vapors by charcoal. One of the main features is that it contains no stopcocks, thereby eliminating the possibility of the adsorption of stopcock grease. Mercury cut-off valves are used in place of the stopcocks.

The methods mentioned above measure the adsorption at constant volume. Occasionally, as in rate measurements, it is desired to measure the adsorption at constant pressure. Taylor and Strother (235) describe such an apparatus. The pressure control is made by raising the mercury level in a reservoir to a height at which the contact between the meniscus of the mercury in the manometer and a tungsten electrode is broken. As the gas is adsorbed, the pressure decreases, and the mercury makes contact with the tungsten electrode. This closes an electric circuit which sends current through an electrolytic cell. The gas generated exerts a pressure on the surface of the mercury reservoir, forcing the gas into a buret and building up the pressure inside, which results in breaking the contact between the tungsten electrode and the meniscus.

The type of data obtained in determining adsorption isotherms is exemplified by the results of Emmett and Brunauer (61) for nitrogen adsorbed on an iron catalyst for ammonia synthesis between −195.8° and −183°C. The curve obtained was the typical S-shaped adsorption isotherm. At low pressures the isotherms are concave, at the higher pressures convex toward the pressure axis. In using such an isotherm in measuring the surface area of the catalyst it is necessary to select the point on the curve corresponding to the completion of a monolayer of adsorbed molecules and to assign a value for the average area covered by each adsorbed molecule. In assigning a value to the average area occupied by an adsorbed molecule, Emmett and Brunauer calculated the diameter of the adsorbed molecules from the densities of the liquefied or of the solidified adsorbate. If the physically adsorbed molecules are close-packed on the surface, the following equation for the average area per molecule is used:

$$\text{Area per molecule} = 4(0.866)\left(\frac{M}{4\sqrt{2}N\rho}\right)^{2/3}$$

where M is the molecular weight of the gas, N is the Avogadro number, and ρ is the density of the solidified or liquefied gas. This equation was derived on the assumption that the molecules are hexagonally close-packed in the solidified or liquefied gas.

Emmett and Brunauer also determined the adsorption isotherms for nitrogen, carbon monoxide, oxygen, carbon dioxide, and butane at temperatures between −195.8° and 0°C. for ten different samples of iron catalysts for ammonia synthesis and discuss the method of obtaining the point corresponding to a monolayer. Brunauer (33) and Emmett (60) in Kraemer's *Advances in Colloid Science* present excellent discussions of the theories involved.

B. Determination of heats of adsorption

In the direct determination of the heat of adsorption both isothermal and adiabatic calorimeters have been employed. In the isothermal calorimeter the heat is allowed to escape from the system and is utilized to produce a phase change such as, for example, the melting of mercury or the evaporation of liquid. The system remains at a constant temperature, and the heat developed is calculated from the amount of solid melted. In the adiabatic calorimeter, the heat is kept in the system, and the amount evolved is calculated from the temperature rise.

Favre (66) was the first to measure heats of adsorption quantitatively, using the isothermal method with mercury as the calorimeter substance. Dewar (55) determined the heats of adsorption of gases on charcoal at −185°C. with the help of a liquid-air calorimeter.

Adiabatic calorimeters have found more favor for the investigation of heats of adsorption in recent years, because they do not restrict the adsorption to one particular temperature. One type of adiabatic calorimeter for low temperature has a platinum resistance thermometer (234) in the center. The adsorbent is in a ring-shaped space surrounding the thermometer. The calorimeter proper is wound with a platinum heating coil used for calibration purposes and is proconstant shows no association for the olefins, but the total surface energy is evidence for slightly higher surface forces. For the acetylenes, no association is manifested and the surface forces are even greater than the olefins. This indication of polarity in simple olefins and acetylenes is borne out by other properties. The temperature coefficient of the dielectric constant has been seen to yield a small permanent molecular moment for unsymmetrically substituted olefins and acetylenes.

Table 4 shows also results obtained with simple oxygenated compounds. Dimethyl ether is the most nearly normal.

Other surface-tension measurements, at low temperatures, have been made by Tonomura and coworkers on toluene, acetone, ethyl ether, methyl alcohol (257), ethyl alcohol, and carbon disulfide (258).

TABLE 5

Temperature range of certain investigations of viscosity at low temperatures

SUBSTANCE	TEMPERATURE RANGE	REFERENCE
Methane	−162 to −183°C.	(187)
Ethylene	−104 to −163°C.	(187)
Ethyl ether, acetone; methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl alcohols	Room temperature to freezing point	(162, 163, 255, 256)
Acetone	Room temperature to −90°C.	(5)
Diethyl ether	Room temperature to −109.8°C.	(6)
Ethylene oxide	Room temperature to −50°C.	(145)

B. Viscosity of liquids

An Ostwald viscosimeter is used. Constant temperatures are secured by use of cryostats of type *c* or *d*. Tonomura (256) uses a viscosimeter with pairs of platinum points at the top and at the bottom as reference marks. He measures the capacity between the points by the method of heterodyne beats and notes when the liquid passes the points by the change of note in the ear phones of the capacity apparatus. In other work, the liquid level is observed through unsilvered strips in the cryostat Dewar.

Table 5 summarizes the compounds which have been studied by various investigators with the temperature range.

C. Spectroscopic measurements

Eisman has described an excellent apparatus for investigation of the absorption spectra of gases and liquids at low temperatures up to pressures of 500 atm. (59).

Methane was found to be transparent in the visible and quartz ultraviolet under all conditions, indicating no association. Ashdown, Harris, and Armstrong have found continuous absorption in the ultraviolet for liquid propylene and cyclopropane at −78°C. (7, 86).

Methods have been worked out for the study of the Raman spectra of liquids boiling below room temperature (80, 129, 233). The liquid is kept below the boiling point in a tube immersed in a simple cryostat, with arrangements for letting the light from the mercury tube be incident on the sides of the tube and for observing the light scattered in the direction of its axis. Oxygen (199), hydrogen chloride (136), ethane, propane, and ethylene (52, 53, 79), methyl chloride and bromide (46, 48), and dimethyl ether (47, 49) have been investigated under these conditions. Harris, Ashdown, and Armstrong have measured the Raman spectrum of liquid cyclopropane (86) at liquid-ammonia temperatures and describe an ingenious apparatus for the purpose.

Conn, Lee, and Sutherland (43) describe an infrared spectrometer to study the change in spectrum with a change in state at a transition point. The infrared-absorption spectrum of hydrogen chloride at liquid-nitrogen temperatures (136) was determined along with the Raman spectrum.

Conant and Crawford (42) have shown that the absorption bands of the porphyrins in the visible are split into finer ones at liquid-air temperatures, owing to reduction of the number of molecules in higher energy states.

Terenin, Yakovkin, and Volobuyev (240) have found that benzaldehyde exhibits fluorescence at −180°C.

The study of absorption spectra of dyes at low temperatures, because of the simpler nature of the spectra, affords evidence concerning the nature of the energy levels in dyes (140, 141, 142). Such evidence is confirmed by a study of the spectrum of the fluorescent light emitted on illumination at temperatures attained with solid carbon dioxide, liquid air, and liquid hydrogen. Terenin (239) has conducted a spectral investigation of the association and photochemical reactions of aromatic compounds at the temperature of liquid air. A convenient apparatus for low-temperature absorption-spectrum measurements has been perfected by Beck (24).

D. *Crystal properties*

The birefringence of a series of organic substances, including all the simple hydrocarbons, has been investigated by Wahl down to liquid-hydrogen temperatures (268, 269, 270, 271, 272, 273). Wahl has detected crystal transition in many cases. This beautiful work is useful in forecasting transitions which will appear in systematic low-temperature specific-heat measurements on simple organic compounds.

X-ray measurements have been made on solid acetylene by Mooy (165). A preliminary interpretation indicates a possible cubic structure with two molecules per cell.

Similar measurements by McLennan and Plummer (154) have been made on methane, indicating a face-centered cubic structure with four molecules per cell (the hydrogen atoms could not be detected).

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LIQUID OXYGEN IN AIRCRAFT[1]

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In passenger aircraft flying above 10,000 ft. large quantities of oxygen have to be carried for breathing purposes. An important reduction in weight can be effected by carrying the oxygen supply in the form of liquid, rather than in gas cylinders. It is then necessary to provide means of evaporating the liquid. Various methods of evaporation are discussed, and the liquid-oxygen evaporator developed at the University of Toronto for the Royal Canadian Air Force is described. In this apparatus the heat of evaporation is obtained from the surrounding atmosphere, and the gas pressure is automatically controlled, so that the rate of supply of gas is determined by demand. Successful test flights have been carried out, including one journey across the Atlantic.

I. INTRODUCTION

The importance of oxygen in high-altitude flight is well known. At altitudes greater than 10,000 ft. the partial pressure of oxygen in normal atmospheric air is insufficient to maintain a human being at full efficiency, except after slow acclimatization. At 25,000 ft. the amount of oxygen is not enough even to support life in the average unacclimatized individual. The problem of supplying the crew and passengers in an aircraft with the requisite amounts of oxygen can be met either by means of a pressurized cabin or by supplying added oxygen directly to the individuals through face masks. Ideally, the pressurized cabin is the preferable solution, since it eliminates other physiological effects of the reduced pressure, as well as that of the lack of oxygen. However, there are obvious objections to the use of pressurized cabins in military aircraft, and even in the transport of passengers the use of oxygen masks is not likely to disappear entirely for some years to come.

In nearly all existing aircraft the oxygen supply is carried in the form of compressed gas in steel cylinders. The weight of the cylinders is five to six times that of the contents, and in large aircraft the weight and bulk become formidable. To take a moderate example, imagine an aircraft carrying twenty-five persons on a flight where provision must be made for a period of 6 hr. at 10,000 to 20,000 ft. At 20,000 ft. the average amount of oxygen required per person is 2 liters per minute (N.T.P.), so that the total amount necessary is 18,000 liters. Allowance being made for the unavailable residue in the cylinders, this requires twenty-two oxygen cylinders of the standard U. S. aircraft type. These make a dead weight of equipment of 396 lb. (exclusive of supporting brackets) and occupy a space of 27 cu. ft.

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II. THE USE OF LIQUID OXYGEN

If the oxygen supply is in the liquid form instead of as compressed gas, a much greater amount can be carried in a given container. At the same time high pressures are not necessary, and lighter containers can be used. Liquid oxygen is preferably stored and transported in metal vacuum flasks, to reduce loss by evaporation. The ratio of the weight of the container to that of the contents is about 2 to 3. However, before it can be used for breathing purposes, the liquid oxygen has to be evaporated, and warmed to a reasonable temperature. In the above example, with a total gas consumption of 50 liters per minute, a heat supply of 150 watts is required for the evaporation alone. This is very much greater than the natural leakage of heat into a properly designed vacuum flask, and a supply of heat must be provided. The evaporator adds to the equipment necessary, but the weight ratio can still be kept at 1 to 1 or better.

The idea of using liquid oxygen for this purpose is by no means new. An experimental, one-man, liquid-oxygen unit was designed by Siebe and Gorman in Great Britain about 1918. However, several factors have prevented it from coming into general use. The early liquid-oxygen evaporators were not entirely fool-proof and required a certain amount of attention in flight. There was danger of the oxygen supply failing, with disastrous consequences. Further, liquid oxygen is always subject to loss by evaporation. In a 25-liter vacuum flask the rate of loss is usually 1 to 1½ liters per day, and it is not economical to store the liquid for longer than about 1 week. This means that it would be necessary to maintain fresh supplies of liquid oxygen at all stopping places. At busy airports, close to large centers of population, this would not be difficult, but it would be a serious problem if the supply had to be maintained at all military airfields. Until the beginning of World War II very few large aircraft were operating regularly at oxygen altitudes, and the saving in weight which could be effected by the use of liquid oxygen was not important enough to overcome these disadvantages. Consequently, experiments on the use of liquid oxygen were abandoned long before 1939, and the use of compressed gas became standard both in the United Nations and in the enemy countries.

Interest in the possibilities of liquid oxygen was revived, both in the United States and in Canada, when large passenger and troop-carrying aircraft were developed, and the prospect arose of using these aircraft on long flights in which it would be necessary to fly at oxygen altitudes, on account of weather conditions or mountainous country. Such flights would take place mainly over established routes, where supplies of liquid oxygen could be arranged if necessary.

When the Royal Canadian Air Force asked the authors to investigate the possibilities of liquid oxygen, it was with this type of service in mind, and the following general requirements were laid down: The liquid-oxygen unit, comprising vacuum container and evaporator, must provide oxygen for twenty-five persons at 20,000 ft. continuously for several hours and, if possible, without attention in flight. At the same time it must be capable of meeting wide variations in demand, with changes in altitude and changes in the breathing rates of individuals. It should allow for an overload of at least twice the normal rate of consumption for short periods, in order to meet the most extreme conditions possible in the aircraft for which it was designed. In order that the liquid-oxygen unit could be used with other standard oxygen equipment,—for example, with R. C. A. F. demand valves,—and be reasonably interchangeable with a compressed-gas system, the oxygen gas must be delivered at a pressure of not less than 25 p.s.i. The evaporator must, of course, continue to deliver gas when the aircraft is subject to acceleration, and when the ambient temperature is as low as −40°C.

The design problem concerns mainly the evaporator and any necessary controls. There are two general methods which might be used to supply the necessary heat,—direct heating by an electric heater immersed in the liquid, or an evaporator separate from the container. Direct electrical heating has been used in a liquid-oxygen unit designed by Mathis and Milan (2) for use in hospitals, and later modified for aircraft. This is the simplest method, but in aircraft application there are objections to the amount of power required and to the fact that the vital oxygen supply is dependent on the maintenance of the electrical power system. Control of the average rate of supply of gas is simple, but an overload results in a drop of gas pressure unless it is soon compensated by increasing the current through the heater.

The special advantage of the separate evaporator is that the heat necessary can be obtained from the surrounding atmosphere, since the temperature of the liquid oxygen is far below the lowest possible atmospheric temperature. The original Siebe–Gorman unit made use of an atmospherically heated external evaporator; the same principle is applied in a unit designed by Akerman (1) and in the unit to be described below. In this type of evaporator the maximum rate at which gas can be supplied depends on the amount of heat which can be absorbed from the surroundings. This may be severely limited by the coating of frost which inevitably forms on the cold evaporator coils.

III. THE UNIVERSITY OF TORONTO–R.C.A.F. LIQUID-OXYGEN UNIT

Figure 1 illustrates the principle of the liquid-oxygen unit designed at the University of Toronto for the R. C. A. F. The container (F) is a 25-liter metal vacuum flask of the usual commercial type. To this the evaporator head and automatic controls are attached. "On-off" valves, master switches, pressure gauges, and the dial of an electrical contents gauge are mounted on a panel accessible to one of the crew. The complete unit weighs 67 lb. empty, and holds 63 lb. of liquid oxygen, producing 19,500 liters of gas, with allowance for the small unusable residue. There is therefore a saving in weight of over 300 lb., as compared with the equivalent in compressed-gas cylinders. At the same time the liquid-oxygen unit occupies a space of only 7 cu. ft.

In order to operate the unit, the flask is filled with liquid oxygen and sealed from the atmosphere, so that the pressure can build up in the space above the liquid, until the required operating pressure is attained (25 to 35 p.s.i. for R. C. A. F. equipment). The operating pressure is the difference between the vapor pressure of the liquid oxygen and the pressure of the surrounding atmosphere. Therefore the temperature of the whole mass of liquid must be raised until it is in equilibrium at the desired pressure. UU in the figure is the evaporator, connected to the liquid oxygen outlet pipe (O), which extends nearly to the bottom of the flask. If the pressure in UU is a little less than that in F, liquid oxygen is forced into the evaporator coils, where it is evaporated by absorption of heat from the atmosphere. The gas leaves the evaporator several degrees colder than the ambient temperature, but by the time it has passed also through several feet of distribution manifold it is warm enough to be breathed.

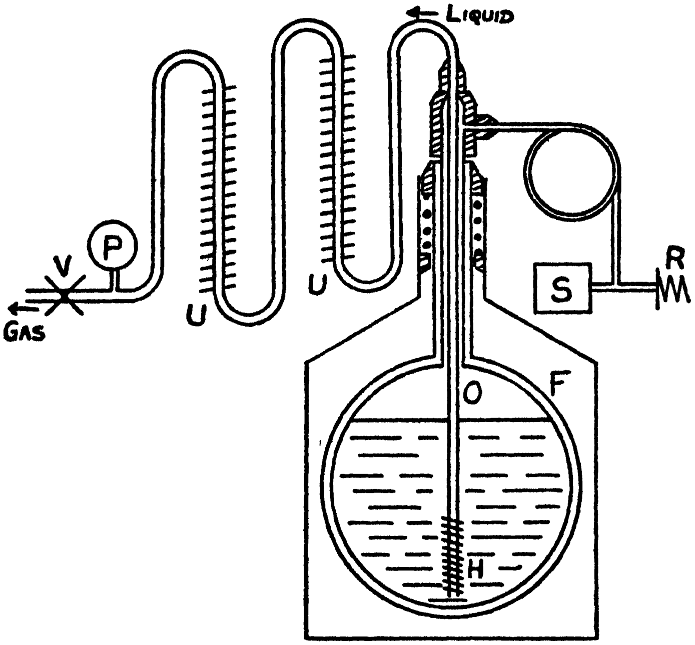

FIG. 1

In a properly insulated vacuum flask of 25 liters capacity the natural heat leak is sufficient only to raise the vapor pressure at a rate of about 1 p.s.i. per hour. Therefore, in order to attain the required operating pressure in a reasonable time, heat must be supplied. Incidentally, it should be noted that the very slow increase of pressure caused by the natural heat leak permits a storage period of 24 to 36 hr. during which there is no loss by evaporation. In order to build up and maintain the operating pressure, an electric heater (H) is wound upon the bottom end of the outlet pipe. This heater is controlled by a pressure-operated switch (S), so that it is turned on automatically whenever the pressure falls below the safe minimum. This, and a spring-loaded relief valve (R), keep the gas pressure between fixed limits as long as the unit is in operation.

The flow of gas is controlled entirely by the various outlet valves in the gas delivery manifold beyond the main control valve (V), for liquid is transferred from the container to the evaporator only as gas is drawn off. Thus the complete system functions as a supply of gas under a suitably controlled pressure, delivering oxygen on demand, up to the maximum capacity of the evaporator.

The evaporator proper consists of two sections (UU) of finned copper tubing, ventilated by means of a small fan or by an air scoop in the side of the aircraft. It will evaporate up to 150 liters of gas per minute, even when the coils are heavily frosted, and when the ambient temperature is as low as −40°C. With higher rates of consumption of oxygen, the liquid tends to surge in the liquid outlet pipe (O) and to splash over from the evaporator into the gas manifold.

At the normal rate of oxygen consumption, 50 to 75 liters per minute, the vapor pressure in the container remains quite steady for several hours at a time, and for normal operation the automatic control of the heater is not essential. However, there is a tendency for the gas pressure to decrease slowly under high rates of consumption, or when the container is nearly empty, and the automatic control is a safety feature. Since the heater is on only during the preflight servicing, and at rare intervals in flight, the drain on the electric power supply of the aircraft is unimportant.

It is interesting to note that the nearly constant pressure is the absolute vapor pressure in the container. Therefore, as the aircraft ascends and the surrounding atmospheric pressure decreases, the gauge pressure of the gas supply increases by an equal amount. This reduces the time required to generate the operating pressure before flight, since a gauge pressure of 21 p.s.i. on the ground will produce an operating pressure of 25.6 p.s.i. at 10,000 ft. On the other hand, this sometimes causes a small wastage of oxygen, since the relief valve may open during an ascent.

IV. TRIALS

Liquid-oxygen units of the type described have been tested on several long flights, culminating in a Transatlantic flight in November, 1944. For this flight two units were installed in the aircraft, and used alternately, in order to provide a sufficient total supply for the longer non-stop legs of the journey. Seven persons actually obtained their oxygen supply from the liquid-oxygen system, breathing through R. C. A. F. demand valves. In addition, whenever the aircraft was at oxygen altitudes, the correct amount of oxygen for twenty-two resting passengers was allowed to blow away. Owing to strong head winds the journey required 24½ hr. of flying time, spread over an elapsed period of 72 hr. Altogether, a period of 15 hr. and 21 min. was spent at oxygen altitudes, mainly at 20,000 ft. The liquid-oxygen system delivered gas continuously whenever necessary, with practically no attention in flight beyond the turning of the taps and switches necessary to alternate units when a container was empty. Thus it was demonstrated in a most satisfactory manner that a liquid-oxygen system is feasible for large aircraft.

The technical development described in this paper was carried out under a grant from the National Research Council of Canada. The flight trials were arranged by the Royal Canadian Air Force and the Royal Air Force Transport Command.

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NEW CRYOGENIC METHODS OF USING LIQUID HYDROGEN[1]

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An apparatus has been developed for producing liquid hydrogen in amounts of 3 to 5 liters for use under conditions where portability and simplicity are important. The liquefier is of the Ahlberg type, operating from ordinary tank hydrogen, purified by passing over charcoal at 90°K. It produces about 1.5 liters of liquid hydrogen in 45 min. from three standard tanks dropped from 2000 to 1000 lb. in.$^{-2}$ A small cryostat has been designed in which a liter of liquid hydrogen will maintain temperatures from 14–20°K. over a period of 20 hr. The cryostat is 14 in. long and 6 in. in diameter. It contains an inner jacket of 1 liter of liquid nitrogen to reduce heat leak to the liquid hydrogen. It is fitted with electrical leads and a rock salt window specially designed for optical studies of superconductors.

I. INTRODUCTION

During the last half-century of physics and chemistry, the use of liquid oxygen and liquid nitrogen has progressed from the stage of a laboratory tool available only in a few specially equipped institutions to a broad field of techniques widely applied both in research laboratories and in industry. On the other hand, the availability of liquid hydrogen or liquid helium is still very restricted. There is increasing evidence, however, that these ultimate refrigerants can be of great help in many fields, especially if they can be produced by apparatus which does not require a person specially trained in low-temperature technique for its operation. Particularly in spectroscopy the possible uses of low-temperature bolometers create a need for simple portable apparatus to produce and maintain temperatures below 20°K. As a first step in filling this need, we have undertaken the development of a light portable liquefier for hydrogen, operating from standard commercial tank hydrogen, and of a small cryostat which can be used in connection with other pieces of apparatus, such as spectrographs, which will maintain temperatures of 20°K. or less for periods of 20 hr. on a single filling with liquid hydrogen. It is the purpose of this paper to describe these pieces of apparatus.

II. THE HYDROGEN LIQUEFIER

Ahlberg, Estermann, and Lundberg (1) some years ago described a small portable liquefier for producing hydrogen from tanks. Our instrument is essentially a further development of that design. It is made up of four functional parts as follows: the controls, the nitrogen-bath unit, the liquefaction unit, and the storage unit. These fit together in a single frame for convenience in transportation.

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[1] Presented at the Symposium on Low-Temperature Research which was held under the auspices of the Division of Physical and Inorganic Chemistry at the 109th Meeting of the American Chemical Society, Atlantic City, New Jersey, April, 1946.

The whole liquefier is shown schematically in figure 1. The liquid-nitrogen reservoir is shown at N. The high-pressure hydrogen gas enters the liquefier through valve V1 at room temperature, after having passed through a purifier, which will be described in a later section. Gauge G1 is a high-pressure gauge which indicates the pressure of the hydrogen gas as it is received from the purifier unit. The gas goes along the high-pressure line (HP) and enters an interchanger (A), located inside the top of the liquid-nitrogen container. The high-pressure gas then goes through a copper coil within the liquid-nitrogen bath, and after that passes through interchanger B to the expansion valve T3. The pressure at this point is roughly 2000 lb. per square inch and is registered on gauge G2. In passing through the expansion valve, the gas drops to a pressure of about 5 lb. per square inch, as registered on gauge G3. There is the usual arrangement for collecting in a Dewar vessel that portion of the gas which liquefies, usually about 10 per cent. The remaining gas passes back through

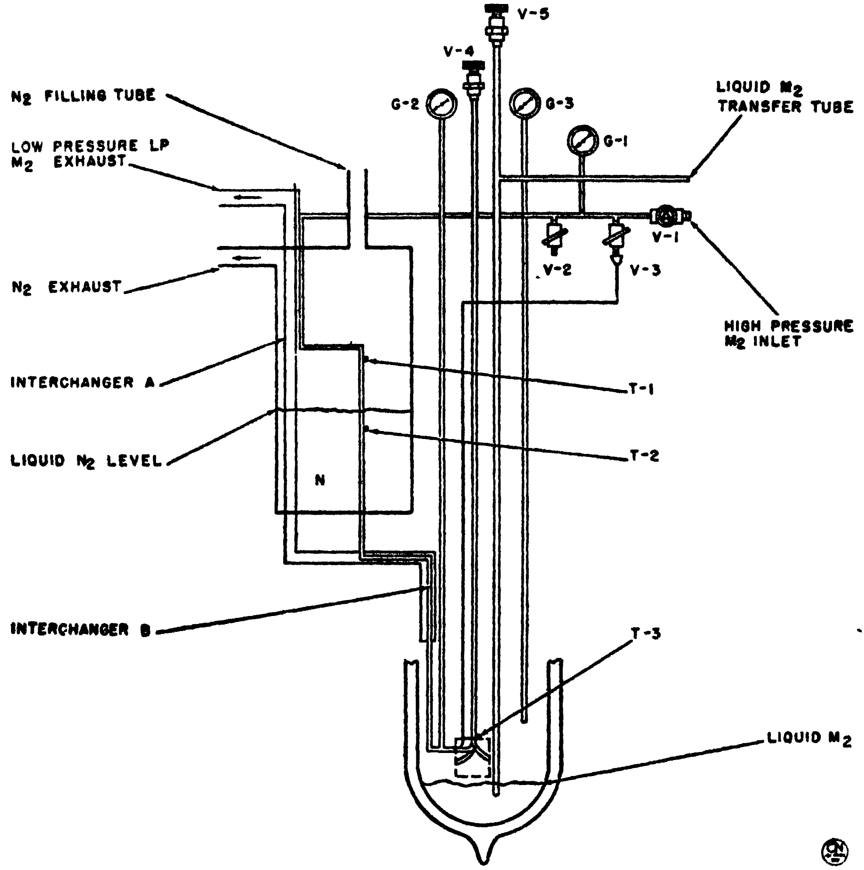

FIG. 1

the interchangers B and A. The percentage conversion to liquid decreases as the pressure falls and is about 3 per cent at 900 lb. per square inch.

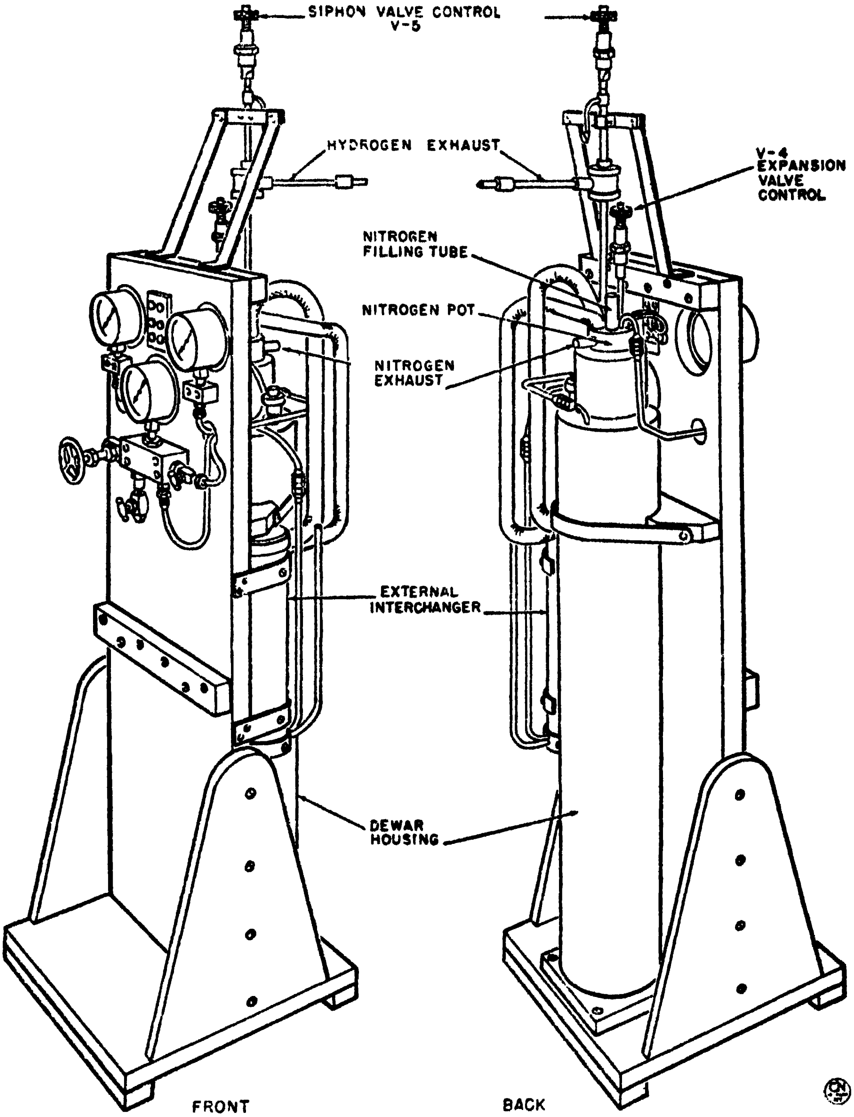

Fig. 2

The assembly of the apparatus is shown in perspective in figure 2. The controls (V1, V2, and V3) and gauges are mounted on the front of the upright wooden panel, which is about 3 ft. high. The liquefier case is on the back, with the two needle-valve controls projecting above. The lower valve (V4)

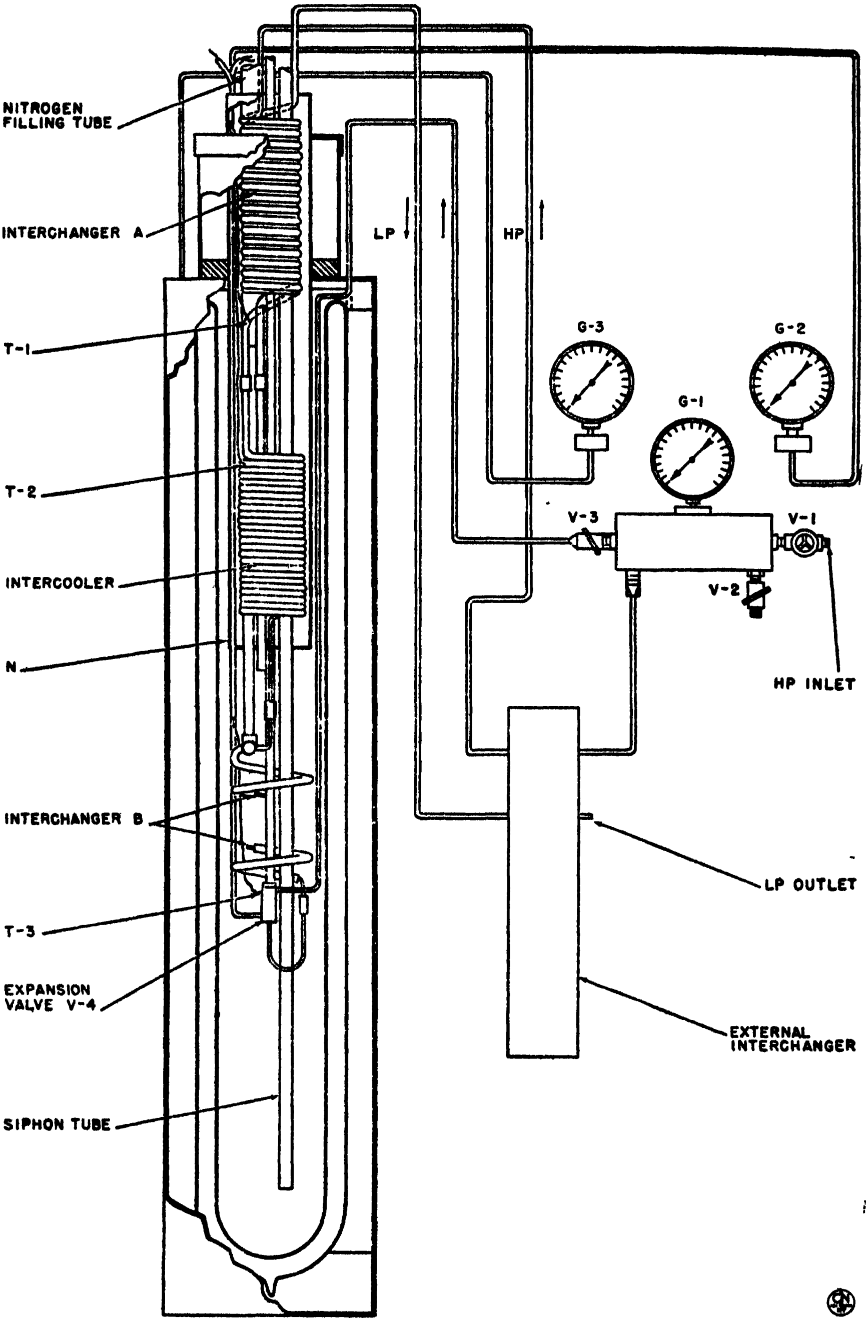
NITROGEN FILLING TUBE
INTERCHANGER A
T-1
T-2
INTERCOOLER
N
INTERCHANGER B
T-3
EXPANSION VALVE V-4
SIPHON TUBE
LP
HP
G-3
G-2
G-1
V-3
V-1
V-2
HP INLET
LP OUTLET
EXTERNAL INTERCHANGER

FIG. 3

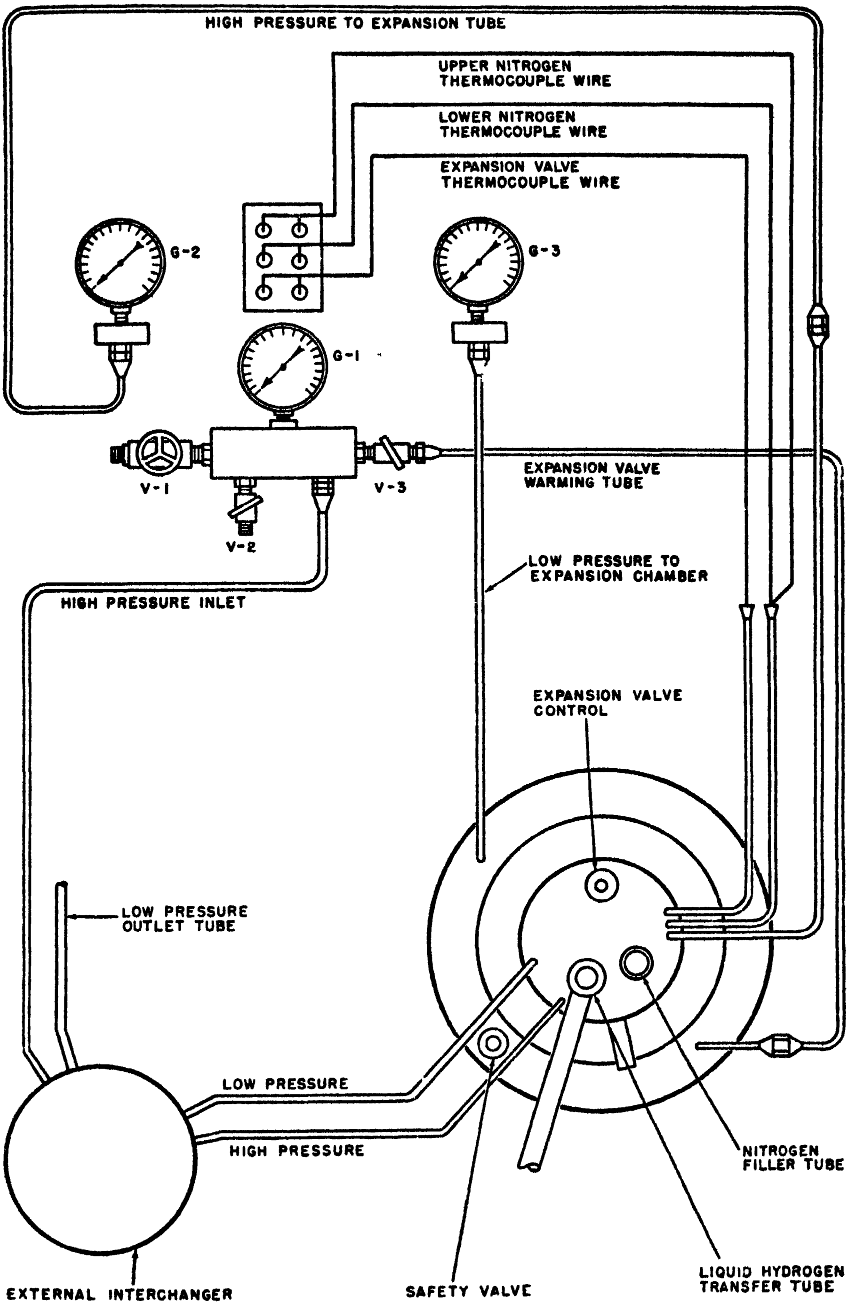
HIGH PRESSURE TO EXPANSION TUBE
UPPER NITROGEN THERMOCOUPLE WIRE
LOWER NITROGEN THERMOCOUPLE WIRE
EXPANSION VALVE THERMOCOUPLE WIRE
G-2
G-3
G-1
V-1
V-3
V-2
EXPANSION VALVE WARMING TUBE
LOW PRESSURE TO EXPANSION CHAMBER
HIGH PRESSURE INLET
EXPANSION VALVE CONTROL
LOW PRESSURE OUTLET TUBE
LOW PRESSURE
HIGH PRESSURE
NITROGEN FILLER TUBE
LIQUID HYDROGEN TRANSFER TUBE
EXTERNAL INTERCHANGER
SAFETY VALVE

FIG. 4

controls the expansion valve and the upper (V5) controls the siphoning off of liquid hydrogen.

Figure 3 shows the main case, with cover partly cut away. Figure 4 shows the distribution of inlet and outlet tubes. Figure 5 shows the detail of the needle valve controlling the siphoning off of liquid hydrogen. Figures 6 and 7 show front and rear photographs of the whole assembly.

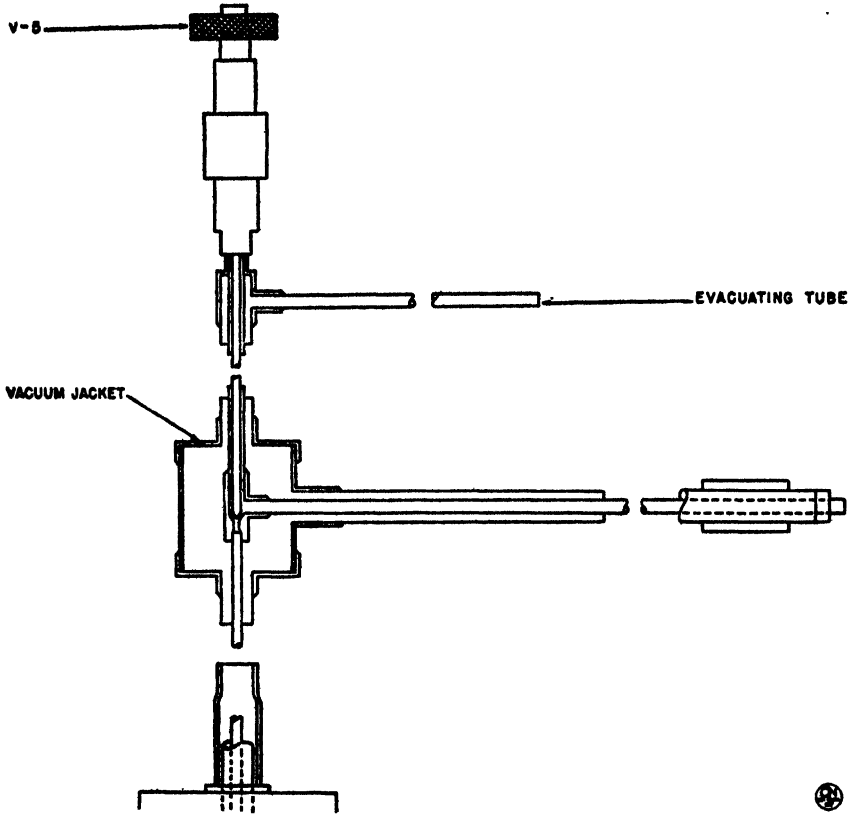

FIG. 5

As shown in figure 3, the first stage of the liquefier consists of a large supernickel tube containing both a coiled double-tube copper interchanger and a single copper tube coil in the nitrogen bath. This will be referred to as the "nitrogen-bath unit". The double-tube copper interchanger is made by soft-soldering side by side a $\frac{1}{4}$-in. copper tube and a $\frac{1}{8}$-in. copper tube. This soldered unit is then formed into a coil small enough in diameter to fit inside the large supernickel housing tube. In the unit shown in figures 6 and 7 an external interchanger was also used, coupled ahead of this interchanger.

The intercooler is made of about 20 ft. of $\frac{1}{8}$-in. diameter tubing wound into a coil so that it also will fit inside the same supernickel housing tube. The small tube of the interchanger is coupled to the intercooler and the two are located, interchanger above intercooler, as shown in figures 2 and 3. The return gas comes from the twisted-tube interchanger and passes directly through a tube in the liquid nitrogen which covers the entire intercooler coil; the return gas tube is then joined to the large copper coil of interchanger A. Soldered to each end of the supernickel housing tube are heavy brass plates, through which all tubes enter and leave the nitrogen-bath unit through soldered connections. This nitrogen-bath unit is supported by a brass disc which is hard-soldered to the outside of the supernickel tube and soldered to the top edge of the main case tube. Around the upper half of the nitrogen-bath unit there is an insulated section made by soldering a brass tube around the supernickel tube and to the support plate. Into the space formed by these two concentric tubes, a filler of hair felt has been packed and a brass cap soldered to the top.

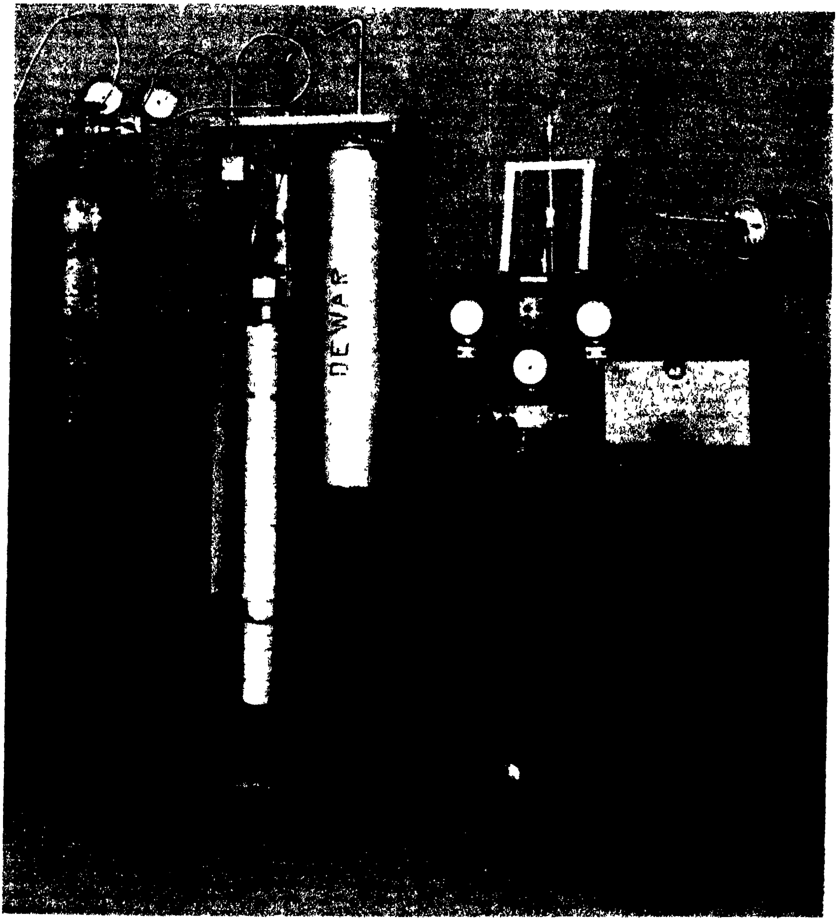

Fig. 6

The interchanger B is soldered, directly below the nitrogen-bath unit, to the $\frac{1}{8}$-in. copper tube that comes from the lower end of the intercooler coil. This interchanger (B) is made by rolling $\frac{1}{8}$-in. O.D. x $\frac{3}{32}$-in. I.D. well-annealed supernickel tubing until a space between the walls has been reduced to 0.005 in. After rolling, this tube is then twisted until there is a lead from one twist to the next of about 1 cm. Each end of this twisted tube for a distance of about 5 in. is left unflattened and untwisted. Over the twisted tube and fitting very closely to it, a lead tube is drawn. This tube is made of lead tubing having an inside diameter of $\frac{3}{16}$ in. and a wall thickness of 0.007 in. A coupling is mounted on one end of the interchanger in such a way that the high-pressure gas may pass through the supernickel twisted tube and return gas may pass around the outside of the twisted tube. The inside of the lead tube is coupled to the return tube which goes through the bottom of the nitrogen-bath unit and through liquid nitrogen, and is then coupled to the $\frac{1}{4}$-in. copper tube of interchanger A. The other end of the supernickel twisted tube then goes to the expansion valve V4, a sensitive needle valve for the control of escaping gas. Packed around the twisted-tube interchanger (B) and tight against the bottom of the nitrogen-bath unit is an insulation made of hair felt held in place by ordinary gauze bandage.

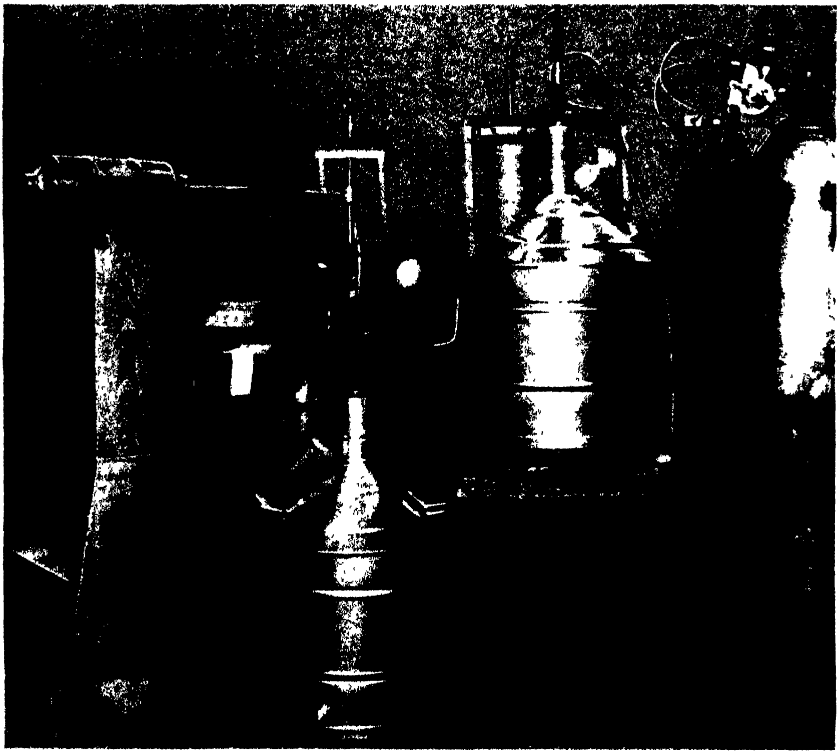

FIG 7

The needle valve V4 is controlled from the top of the liquefier by means of a double-walled, gas-tight, supernickel tube arrangement. This whole unit, comprising the lower portion of the nitrogen-bath unit and the twisted-tube interchanger and expansion valve, is encased in the glass Dewar vessel. The siphoning of liquid hydrogen from the Dewar is controlled by the valve shown in figure 5, vacuum jacketed as indicated. Around the Dewar vessel and insulated from it by hair felt is a brass cylindrical jacket to the top of which is soft-soldered the support flange of the nitrogen-bath unit. Into this flange is mounted a safety valve to relieve any sudden increase of pressure which may build up in the expansion chamber (see figure 2). There is also a tube leading from this flange to a pressure gauge which indicates the internal pressure of the expansion chamber. Soldered through this flange is a small-bore supernickel tube which can lead hydrogen directly from room temperature to the expansion valve seat for the purpose of warming the expansion valve in the event of the formation of a frozen plug of impurity at that point.

All gauges and valves, with the exception of the expansion valve and the transfer valve, are mounted on the wooden panel which forms the stand of the complete unit (figure 2).

III. THE PURIFIER

Our experience has been that standard commercial hydrogen, as received in the usual cylinders, is not of sufficient purity to be suitable for use in our liquefier. There is usually enough impurity of one sort or another to cause clogging after a relatively short period of operation. We therefore place a purifier unit in the line between the source tanks and the liquefier. It is shown diagramatically in figure 8a. It consists, essentially, of two parts: an activated silica gel trap, and an activated charcoal trap, the first of which removes water vapor and any other easily condensible gas, and the second, traces of oxygen and nitrogen. The tube connecting the two traps between B and C can be removed by unscrewing the compression fittings. Details of the traps are shown in figure 8b.

The silica gel trap may be activated in two ways, depending on whether or not compressed air is available. In the first method the heater is connected to a 110-volt source and a slow stream of air is passed in at the point C (figure 8a) with valve V6 open. This hot air then passes through the silica gel trap and produces a desorption of air from the silica gel surface. The air emerges at V6. About 8 hr. are required to activate the silica gel. In the second method, a vacuum pump is connected to the system at C, valve V6 being closed. Heat for desorption is again supplied by the heater. Evacuation should be continued for about 6 hr., and the vacuum pump is protected by a cold trap.

The charcoal trap is activated by evacuation through B, with valve V1 closed. Heat is supplied to the trap by means of a specially constructed heater which can be slipped into place, replacing the Dewar vessel.

Figure 6 shows, reading from left to right, a stand and tank of hydrogen, the purifier, the liquefier (front), and a cryostat (rear view). In the rack which contains the purifier traps, the heater for the charcoal is kept in a pocket at the lower part of the rack, as is shown in figure 6. The heater is equipped with a copper–constantan thermocouple. When in operation the heater is connected to a source of electric power at 110 volts until the temperature of 150–180°C. is maintained. When the silica gel trap is being evacuated simultaneously, the heaters on the two traps are connected in parallel. After heating the charcoal trap for 6 hr., it is allowed to cool under continuous pumping. It is flushed with hydrogen gas before being used again.

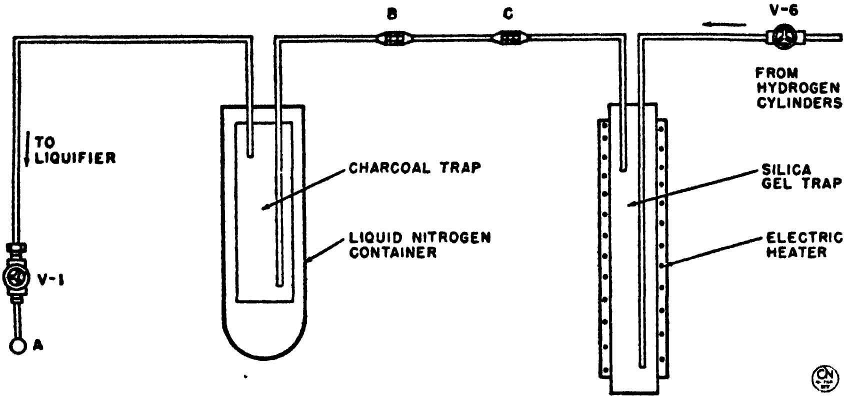

FIG. 8A

IV. CRYOSTAT

In order to provide a chamber for experiments at liquid-hydrogen temperatures with apparatus such as the superconducting bolometer, we have developed a relatively small cryostat in which temperatures between 14° and 20°K. may be maintained for periods up to 20 hr. This cryostat is shown schematically in figure 9. It is made up of a series of nested copper cans spun from copper of wall thickness about 1 mm. The outer case (A) is about 25 cm. long and 12 cm. in diameter. This serves as the vacuum jacket, the vacuum being maintained by the action of the liquid hydrogen inside the inner can, labeled N. This can has a volume of approximately 1000 cc.

A hollow tube passes through N from top to bottom at its center. Within this tube and soldered to it at the bottom there is a copper post (M) made of tubing of ⅜-in. O.D. and ¼-inch. I.D., which is about 2 cm. longer than the hydrogen can and consequently extends out at the top. To the top of this post there is soldered a plate to which the bolometer base, S, is normally attached with low-melting solder. Wound around the post at M is a bolometer-sensitizing coil, made of No. 40 constantan wire, and approximately 500 ohms in resistance. A current passed through this coil raises the temperature of the top of the post and of the bolometer a few tenths of a degree above the temperature of the hydrogen in the can N.

Normally, for bolometer operation, the hydrogen in can N is kept under reduced pressure such that part of it will stay in the frozen state. Thus the can

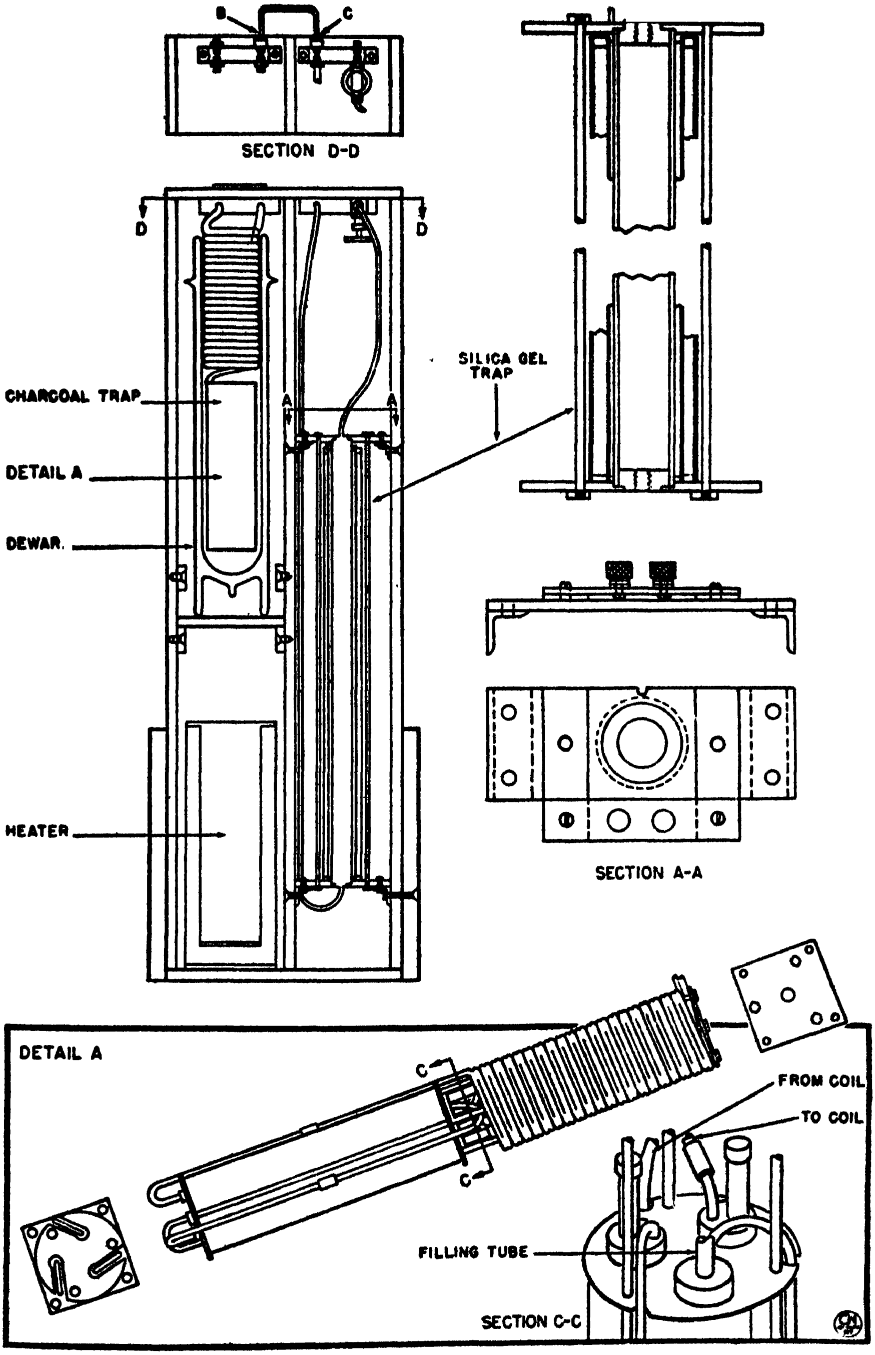
B
C
SECTION D-D
D
D
CHARCOAL TRAP
DETAIL A
DEWAR
HEATER
SILICA GEL TRAP
A
A
SECTION A-A
DETAIL A
C
C
FROM COIL
TO COIL
FILLING TUBE
SECTION C-C

FIG. 8B

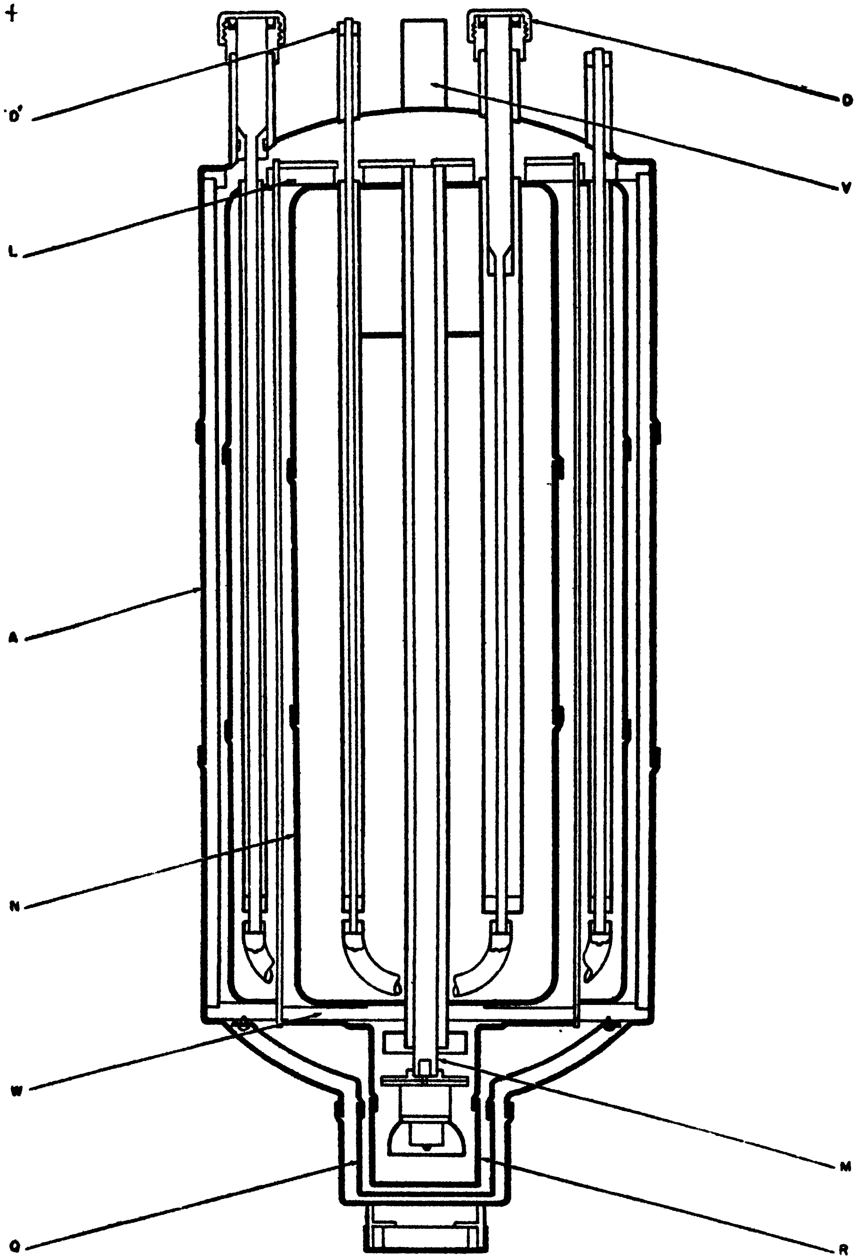

Fig. 9

will have a temperature of 14°K., and the bolometer can be raised to its proper operating temperature, usually about 14.5°K., by means of the current passed through the constantan coil. When the current through the heating coil is set at the proper value, the bolometer will remain in its sensitive state as long as the supply of hydrogen lasts in the can, with perhaps an occasional adjustment of temperature every 5 hr. or so.

The can is filled with liquid hydrogen through the tube D, which is a supernickel tube having an outside diameter of $\frac{3}{16}$ in. and a wall thickness of 0.010 in. The outer end of the tube is equipped with a screw cap which will clamp down on the rubber washer and grip tightly the glass transfer tube through which the liquid hydrogen passes into the can. A supernickel tube of $\frac{1}{4}$-in. outside diameter and 0.010-in. wall thickness, shown as D′ in the diagram, acts as a vent tube while the can is being filled. It also serves as a tube through which the space above the surface of the liquid hydrogen can be pumped to reduced pressure in order to obtain the triple-point mixture. Surrounding the liquid hydrogen can there is a double-walled can containing liquid nitrogen and having a volume of approximately 400 cc. This can provides a thermal dam which cuts down the heat leak into the liquid hydrogen from either radiation or conduction. It normally contains liquid nitrogen at the boiling point, 77.4°K. The inlet and outlet tubes ($\frac{3}{16}$-in. O.D., 0.010-in. wall thickness) for filling with liquid nitrogen are equipped similarly to the tubes on the hydrogen can.

Within these cans the tubes come up to the top facing each other, as shown in the diagram. Thus, when a can is nearly full of liquid refrigerant, it may be held either horizontally or vertically without spilling. These cans are held in place within the outer casing (A) by means of masonite spacers $\frac{3}{16}$ in. thick, marked L and W. These serve as insulator rings between the hotter and colder parts of the apparatus. It is found that when the whole apparatus is cooled, the occluded gas in the masonite is not a significant factor in damaging the vacuum. The thermal insulation is very good, as indicated by the figures on the heat leak quoted later. On the other hand, the spacers have sufficient mechanical rigidity so that the whole can will withstand vibration equivalent to a strain of 10 g. In order to provide protection from radiation, two shields are provided (Q and R). Above the radiation shields, the top of the cryostat is equipped with a rock salt window through which infrared radiation may be admitted to a bolometer.

Wires to provide the electrical leads to the bolometer and to the bolometer-sensitizing coil wound on the post enter through a vacuum-tight connector located at the bottom of the cryostat but not shown. The connector is made of an ordinary eight-prong metal radio tube, which is cut off and soldered into a hole in the cryostat. A tube (V) is provided for a preliminary evacuation of the cryostat, if desired.

In order to improve the vacuum, two cylindrical charcoal containers are placed in reëntrant tubes in the nitrogen can, so that a relatively high vacuum is produced as soon as the nitrogen can is filled. The action of these containers plus the condensing action of the liquid hydrogen in the hydrogen can is such that a vacuum can be maintained for several days, even though the evacuating tube (V) is closed off with an ordinary piece of rubber tubing and a pinch clamp. The weight of the cryostat and its over-all dimensions are as follows:

Weight of copper cryostat, empty	10.7 lb.
Maximum diameter	5.2 in.
Over-all length, tip of window frame to end of electrical plug	15 in.
Longest external tube projection (nitrogen inlet and exhaust tube)	1.0 in.
Length of electrical plug	$1\frac{3}{8}$ in.
Weight of liquid nitrogen, 900 cc. (density, 0.80 g./cc.)	1.6 lb.
Weight of liquid hydrogen, 1050 cc. (density, 0.07 g./cc.)	0.16 lb.
Total weight of cryostat when completely filled	12.5 lb.

The heat leak into the hydrogen can, measured by observing the amount of gas which evaporates from it, has a value of approximately 0.3 watt. The heat leak into the nitrogen can is about 3 watts.

V. OPERATION OF COMBINED UNIT

The liquid-nitrogen containers on the liquefier, purifier, and cryostat are first filled. The level of liquid nitrogen in the liquefier is observed by means of a thermocouple. Gaseous hydrogen at approximately 2000 lb. is then admitted to the liquefier. Approximately ½ hr. after the hydrogen has been flowing through the liquid nitrogen, significant liquefaction will begin. This is indicated when the reading of thermocouple T reaches a steady value at the appropriate amount above the value shown by the thermocouples immersed in the liquid nitrogen. It is not economical to continue liquefaction after the pressure falls from 2000 to below 900 lb.

Liquid hydrogen is transferred from the liquefier into the cryostat through a double-walled glass Dewar transfer tube. It is accomplished merely by opening the valve at the top of the liquefier to the proper amount such that the over-pressure in the liquefaction chamber will force the liquid up the siphon and into the cryostat.

If the hydrogen gas should contain impurities which get past the purifier, or if the purifier is not working properly because of a failure to bake out sufficiently, clogging may take place at the main expansion valve. This can be remedied by by-passing some of the room-temperature hydrogen through the valves provided for that purpose, past the expansion valve, thus warming it. As a rule, a few minutes of by-passing hot gas is sufficient to melt and blow out any impurities.

In order to show the length of time involved in the different steps of operation, typical data are presented in table 1.

The units described in this paper were developed over a considerable period by a large group working on a combined project during the years 1942–46. While the authors of this paper had perhaps the greatest experience with the finished

TABLE 1

TIME *hr. min.*	REMARKS
0	Cylinder manifold connected to inlet of purifier unit. One cylinder at 2000 lb. open to purifier; inlet valve to liquefier closed. Began cooling charcoal trap of purifier with liquid nitrogen.
0:05	Charcoal trap cold; opened high-pressure inlet valve V1 to liquefier. Adjusted expansion valve until low-pressure gauge (G3) showed 2 lb. in expansion chamber.
0:06	Began adding liquid nitrogen to reservoir of liquefier.
0:08	E.M.F. of thermocouple T2 steady at 6.2 millivolts.
0:10	E.M.F. of thermocouple T1 steady at 6.2 millivolts. Stopped adding liquid nitrogen. E.M.F. of T3 is now 2.0 millivolts.
0:20	T3 reads 2.5 millivolts.
0:30	T3 reads 5.7 millivolts. Liquefaction beginning. Pressure in single cylinder has now dropped to 700 lb. Three full cylinders connected to purifier unit. Total pressure 1900 lb.
1:00	G1 and G2 = 950 lb. G3 = 4.8 lb. 5-min. transfer.

Note: This was sufficient to cool and completely fill one cryostat.

units, the larger part of the credit for their construction and successful operation should be distributed among those who participated in the earlier stages of the project, not all of whom were able to share in the final successful operation. In particular, acknowledgement is made to Dr. E. R. Blanchard, Dr. W. T. Ziegler, Dr. J. W. Hickman, Dr. C. L. Christ, Mr. William Corak, and especially to members of the engineering staff, Mr. W. R. Asher and Mr. H. W. Bittner.

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(1) Ahlberg, J. E., Estermann, I., and Lundberg, W. O.: Rev. Sci. Instruments **8**, 422 (1937).

A SUPERCONDUCTING BOLOMETER FOR INFRARED MEASUREMENTS[1]

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Received October 1, 1946

A sensitive high-speed bolometer, operating at about 16°K., has been constructed which will give detectable signals from an impulse of radiation 1.2×10^{-4} sec. long, containing 2×10^{-6} ergs of energy, using a wide-band pass amplifier. The sensitive element is a ribbon of columbium nitride, 0.125 in. x 0.010 in. and 0.001 in. thick, which has a superconducting transition 0.07° wide at 15.8°K. The nitride, which serves as the receiver, is bakelited to a copper block which, by means of an electric heater and hydrogen at its triple point, is maintained at a constant temperature such that the columbium nitride is in the steepest portion of its resistance–temperature curve. At this point, values of dR/dt may run from 1 to 100 ohms deg.$^{-1}$ The bolometer is used in a bridge circuit with 10 milliamperes of current; the first stage of amplification is a transformer (1-ohm primary impedance, 1.1-megohms secondary impedance); the second stage is a conventional wide-band audio amplifier. The peak noise level of the apparatus is equivalent to 0.025 microvolt at the bolometer level. Frequency response curves for sine- and square-wave radiation inputs have been obtained. The energy source employed is an oxidized iron plate kept at 100°C.

I. INTRODUCTION

Infrared radiometry in the middle 1930's was in the position that the detectors then used had been perfected to the stage where the factor limiting their sensitivity was Brownian motion or a related effect (5). The most sensitive detectors had their limits of detection at a flux of about 10^{-3} ergs sec.$^{-1}$, and time constants ranging from 1 to 10 sec.

In 1938 (1) and 1939 (10) it was pointed out that superconductivity offered an excellent means for measuring very small quantities of energy. A superconductor being used as a bolometer, temperature coefficients of resistance could be increased by many orders of magnitude, thermal capacities would fall to very low values, and statistical fluctuations would be reduced with the absolute temperature.

The first results obtained with superconducting bolometers showed a minimum detectable flux of about 10^{-3} ergs sec.$^{-1}$ with a 10-sec. time constant (2, 3). The superconductor was a coil of tantalum wire refrigerated by a helium bath, boiling under reduced pressure at 3.22°K. The factor limiting the sensitivity of this instrument was the temperature fluctuation of the helium bath.

Soon after this there arose a need for an infrared detector of similar sensitivity at about 10 μ but with a time constant equal to or less than 0.001 sec., and with the emphasis on handling isolated short-duration energy pulses. It was toward this end that this work on the superconducting bolometer was directed.

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[1] Presented at the Symposium on Low-Temperature Research which was held under the auspices of the Division of Physical and Inorganic Chemistry at the 109th Meeting of the American Chemical Society, Atlantic City, New Jersey, April, 1946.

[2] This article is based upon the dissertation submitted to the Faculty of the Graduate School of Johns Hopkins University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1944.

In 1941 (4) and independently in 1942 (11) it was found that columbium nitride was a superconductor in the region above 14°K. This discovery opened the way to a solution to the temperature fluctuations of the refrigerating bath. By utilization of the triple-point mixture of hydrogen at 14°K., obtained by pumping on the vapor above boiling hydrogen, as a temperature sink for a superconducting bolometer of columbium nitride, the background temperature fluctuations could be very greatly reduced. The bolometer could be raised to the appropriate operating temperature by an electric heater placed between the bolometer and the sink. It was along these lines that the development proceeded.

II. PREPARATION OF COLUMBIUM NITRIDE

The first papers (4, 11) on the superconducting properties of columbium nitride did not agree on the position and width of the transition or on the method of preparation. These disagreements had to be cleared up, and in such a manner as to yield small-dimension, electrically conducting columbium nitride specimens with very sharp superconducting transitions.

A new nitriding method was chosen. It called for the heating of columbium metal by the passage of current through it while suspended in a stream of ammonia. It was hoped that if ammonia were used instead of nitrogen the temperature might be lower and the time shorter than otherwise. The method proved successful and will reproducibly yield columbium nitride with transitions at 15.9°K. ± 0.1° and 0.15 ± 0.04 degrees wide. A strip of columbium metal[3], 20 cm. long, 6 mm. wide, and either 0.0254 mm. or 0.0063 mm. thick, is suspended tautly in a slowly flowing stream of dry ammonia. Current is passed through the metal and it is maintained thus for 20 min. at temperatures between 1350°C. and 1500°C., as read with an optical pyrometer with no emissivity correction.

A second method, using a stationary atmosphere of purified nitrogen in place of the ammonia, has been tried. The temperature is kept at 1500°C. for 1 hr. The results are not strictly reproducible but the transitions usually lie between 14°K. and 15°K. and the transition widths vary from 0.03° up. A more complete report on this has appeared (14). Figure 1 is a plot of resistance against temperature for several specimens of columbium nitride. Curve a is for a typical preparation in ammonia, while curves b and c are for two different samples prepared in nitrogen.

III. BOLOMETER CONSIDERATIONS

If the signal from the bolometer is amplified without any distortions, the resulting signal, $\Delta\phi$, as observed on a cathode-ray screen or other instrument, will be

$$\Delta\phi = a\Delta iR = ai\Delta R = aiR\left(\frac{1}{R}\frac{dR}{d\theta}\right)\Delta\theta \qquad (1)$$

---

[3] Obtained from the Fansteel Metallurgical Company, Chicago, Illinois. The impurities (mostly oxygen) = 0.2 per cent.

where a is the factor of amplifications, i the current through the bolometer, R the resistance of the superconductor when in operating condition, $\frac{1}{R}\frac{dR}{d\theta}$ or ρ the temperature coefficient of resistance, and $\Delta\theta$ the increase in temperature of the bolometer.

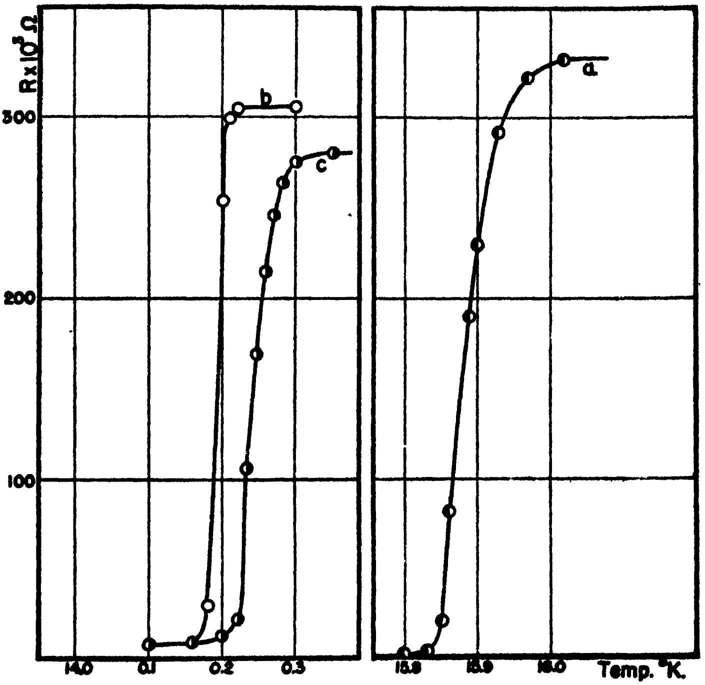

FIG. 1. Resistance *versus* temperature. Columbium nitride superconducting transitions. Curve a, sample prepared in ammonia; curves b and c, samples prepared in nitrogen

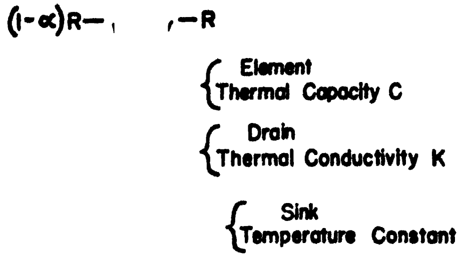

FIG. 2. Idealized thermal diagram

Consider first the temperature rise, $\Delta\theta$. Let us assume simply, as in figure 2, that radiation falls on an element with the heat capacity c, that fraction α of it is absorbed, that the conductivity of this element is such that there are no appreciable temperature gradients in it, that a thermal drain of conductivity k

and negligible thermal capacity connects the element to a constant temperature sink, and that there are no radiation losses. If θ represents the temperature of the element, at least part of which is the superconducting element, and $\theta_0 = 0$ the temperature of the sink, we can determine θ as a function of c and k and the characteristics of the radiation wave.

If radiation of intensity J falls on the detector, starting from $t = 0$ we have:

$$\theta = \frac{\alpha J}{k}\left(1 - e^{-\frac{k}{c}t}\right) \tag{2}$$

Figure 3 shows a plot of this equation and gives the $\Delta\theta$ for a short-duration energy pulse.

If the radiation has the following form:

$$R = I + I \sin\left(2\pi ft - \frac{\pi}{2}\right) \tag{3}$$

where f is the frequency of the sine wave, the equation for θ can be obtained. To simplify this equation we consider two extremes, one when

$$k \gg 2\pi fc$$

and

$$\theta = \frac{\alpha I}{k}\left(1 + \sin\left[2\pi ft - \frac{\pi}{2}\right]\right) \tag{4}$$

and the other when

$$k \ll 2\pi fc$$

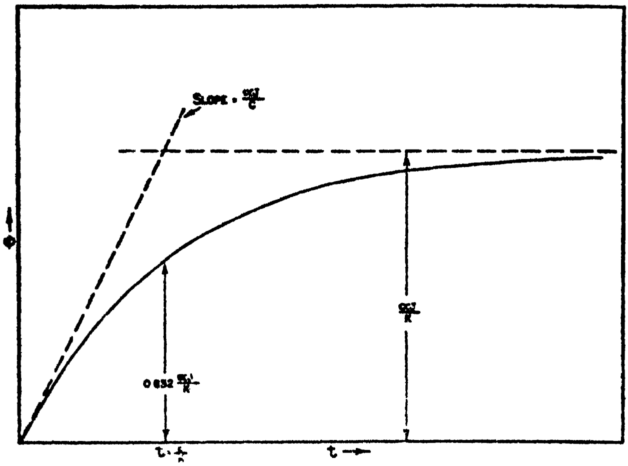

FIG. 3. Graphical representation (solid curve) of the equation

$$\frac{\alpha J}{k}\left(1 - e^{-\frac{k}{c}t}\right)$$

Broken lines are asymptotes.

and

$$\theta = \frac{\alpha I}{2k} - \frac{\alpha I}{2\pi f c} \cos\left[2\pi f t - \frac{\pi}{2}\right] \tag{5}$$

A log–log plot of the equation for which equations 4 and 5 are the asymptotes is represented by figure 4. For the heat system which we have described, the time constant is defined as $t_c = c/k$, and its importance for the two types of radiation signals described is made clear from figures 3 and 4.

From the above analysis it is seen that in order to obtain a maximum $\Delta\theta$, α should be as near 1 as possible, c as small as feasible, and k so chosen that c/k is equal to the duration of the radiation pulse for which the instrument is designed, or so that $k = 2\pi c f_c$, where f_c is the frequency in which one is interested. Larger values for k will decrease the $\Delta\theta$ almost linearly; smaller values will not appreciably increase the temperature rise, except when the duration of flash is longer, a condition generally disadvantageous.

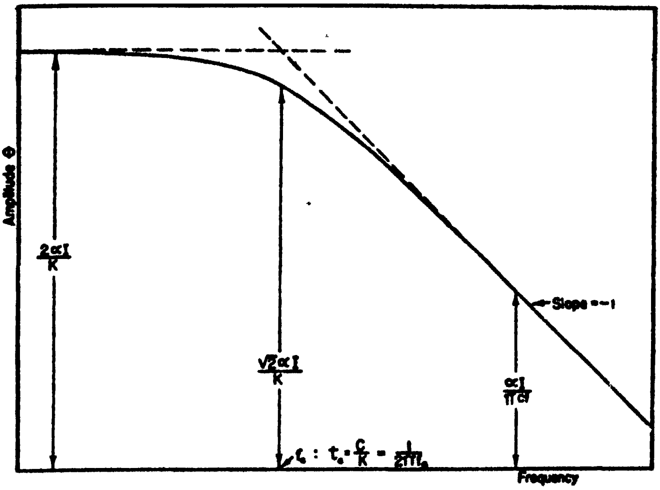

FIG. 4. Plot of the total amplitude of the temperature oscillation against frequency of sine-wave radiation on log–log paper.

According to equation 1 the signal should be proportional to the current. However, there is a limit to the current that can be passed through the bolometer, because the i^2R heat must be conducted away by the drain. It is evident that if the maximum slope of the curve of i^2R against temperature for the bolometer is larger than k, thermal instability will result and it will not be possible to operate the bolometer at the point where $dR/d\theta$ is largest and the detector most sensitive. For a given bolometer then, the current should be adjusted until the following equation nearly holds:

$$k = i^2R\rho_{\max}. \tag{6}$$

To use higher currents, k would have to be increased or R and $\rho_{\max}$. decreased, but since i appears as the square, these would lead to reduced signals.

The signal is directly proportional to ρ. The maximum value of ρ is determined by the width of the superconducting transition, assuming that the shape of this curve is similar for all samples. Thus sharper transitions are desirable, but the signal is not increased proportionally because equation 6 must hold. As ρ is increased, i^2 must be decreased and the effect on the signal is thus $(\rho_2/\rho_1)^{\frac{1}{2}}$. Similar considerations hold for R, so that changes in the resistance of the element affect the signal as $(R_2/R_1)^{\frac{1}{2}}$. The value of R is changed by the physical dimensions of the superconductor.

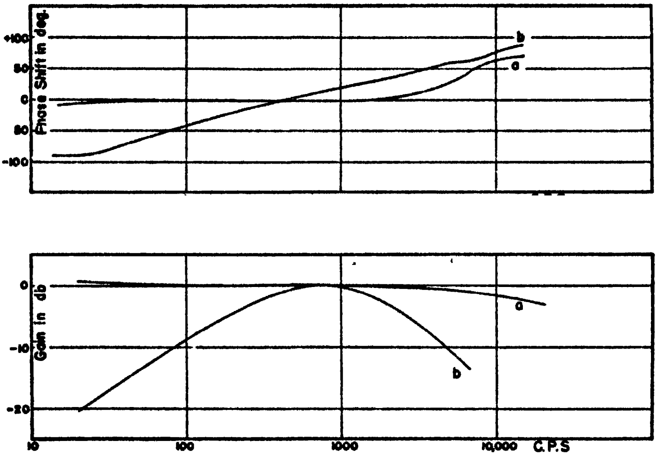

FIG. 5. Phase shift and relative gain of amplifier: (a) without transformer; (b) with transformer.

Equation 1 assumes that we can take any voltage change and amplify it by a factor a without any distortions. This can usually be done, but in general, amplification is only carried to the point where noise levels are seen. The average vacuum-tube amplifier with a band pass of 20 to 20,000 c.p.s. will have a noise level, due to shot and grid resistor noises, at the first tube of from 2 to 20 microvolts. As will be shown later, the thermal noise in the bolometer itself is about 2×10^{-3} microvolts. To make as much use of this low level of noise as possible, a specially built high-gain transformer was placed between bolometer and amplifier. The transformer had a split primary of 1-ohm impedance and a secondary of 1.1-megohms impedance. With this in the amplification circuit, equation 1 is no longer strictly valid. Figure 5 shows the extent of the frequency and phase distortion thus introduced. Figure 6 is the complete amplification circuit. The bolometer is placed in one arm of a bridge, opposite an equal resistance dummy, and the connections to the primary are such that extraneous disturbances cancel out.

IV. BOLOMETER CONSTRUCTION

For three reasons it seemed wise to make the superconducting element itself the receiver: (*1*) heat capacity was kept at a minimum; (*2*) it was difficult to obtain an adhering blackening agent at these low temperatures without short circuiting the element; and (*3*) the highly granular surface of the columbium nitride indicated that it might be not too poor an absorber of infrared radiation. The element was made as thin and narrow as was feasible, considering the difficulty that was encountered in handling the brittle nitride.

Since the temperature at every point on the superconducting detector must be the same if the maximum $dR/d\theta$ is to be realized, the i^2R heat generated in the detector and the radiant energy it absorbs must be conducted away from every unit section of the element with equal facility. This, plus the fact that to obtain such a small time constant would require a large thermal conductivity, led to the binding of the entire lower surface of the superconducting element to a massive copper bar, whose end was immersed in the hydrogen. A thin layer of an electrically insulating adhesive was used for this purpose. Although several adhesives were tried, bakelite lacquer[4] was finally chosen because of its ease of application and its ability to withstand the differential expansions and hold securely at very low temperatures.

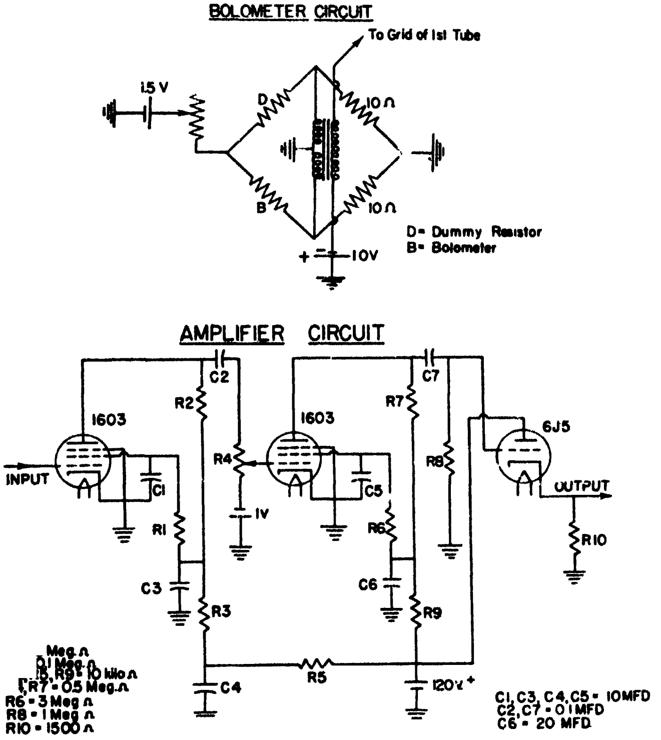

FIG. 6. *Bolometer and amplifier circuits*

In its final form, the element was a piece of columbium nitride, 6.35 mm. long, 0.254 mm. wide, and either 0.0254 mm. or 0.0063 mm. thick, that had been cut from the nitrided foil. Each end was copper plated for a length of 1.6 mm., using an acid copper-plating solution and very low current densities to obtain an adherent plate. These ends were wet with a zinc chloride–hydrochloric acid flux and immersed in a molten bead of solder,[5] care being taken not to heat the solder much above its melting point, as extreme heat tends to loosen the copper plate.

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[4] Bakelite lacquer BL 3128 from the Bakelite Corporation, Bound Brook, New Jersey.

The bolometer base was a 6.35-mm. square copper bar, surrounded by a protecting cup. Two 36 B. and S. gauge copper wires, bakelited to this cup, made electrical connection with the element. The top of the copper bar was smoothed with crocus cloth and a thin layer of bakelite lacquer applied. This was air dried for 4 hr. and then baked at 140°C. for 5 hr. This process was repeated (usually once or twice) until the desired thickness of insulator was obtained.

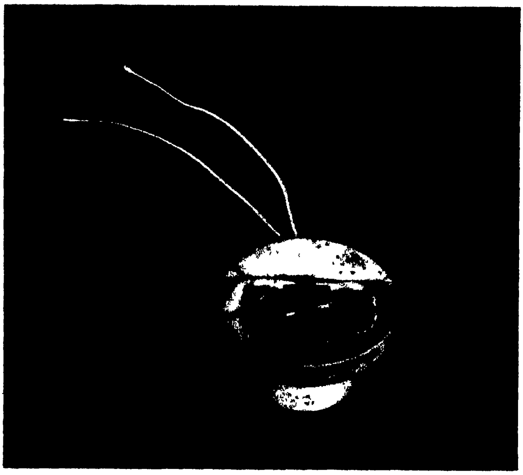

FIG. 7. The bolometer

The columbium nitride element was finally placed on top of a freshly applied coating of lacquer and gently pressed down to insure wetting of the entire lower surface. This was air dried for 1 day and then baked at 140°C. for another.

If any bakelite ran over the top surface it was removed after baking by scraping gently with a sharp instrument. The lead wires, tinned and fluxed, were brought into position and soldered to the element with a touch of the soldering iron. Figure 7 is a photograph of a bolometer.

The resistance of an element 0.0254 mm. thick is about 0.4 Ω just above the superconducting transition. The resistance of the thinner element is four times this value.

V. BOLOMETER TESTING

The source of radiation was a wrought-iron plate, whose front surface had been oxidized by heating to red heat in the air and on whose back surface was cemented a nichrome heater. The temperature was read by a chromel-alumel thermocouple. The form of the radiation curve was determined by the chopping wheel placed directly in front of the source and the shutter placed immediately in front of the wheel. The light paths were so designed that the only variable radiation that was impinging on the bolometer came through the shutter. All the energy that hit the bolometer through the shutter came either from the aluminum chopping wheel or from the heated iron plate. Two wave forms were used: a sine wave, and a square pulsed wave with the radiation off forty-eight times as long as it was on.

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[5] One part of lead to one part of tin.

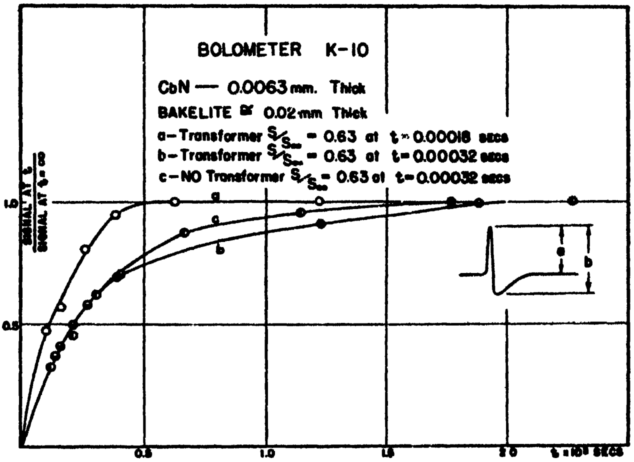

FIG. 8. Response of bolometer K-10 to square-wave input as a function of duration of flash.

In this last type of wave the equation for the change in radiation hitting the bolometer is:

$$Q/t = \frac{A_1 A_2 \sigma (\alpha_1 \beta_1 T_1^4 - \alpha_2 \beta_2 T_2^4)}{\pi d^2} \tag{7}$$

where A_1 is the area of the shutter, A_2 the area of the bolometer, σ the radiation constant, α_1 the black-body coefficient for the oxidized iron surface, β_1 the fraction of the thermal radiation from T_1 passing the rock salt window in the cryostat, T_1 the temperature of the heated source, α_2, β_2, T_2 the same quantities for the aluminum wheel, and d the distance between bolometer and shutter.

The most sensitive bolometer used in these studies, K-10, was made with a columbium nitride thickness of 0.0063 mm., a bakelite thickness of approximately 0.02 mm., and a transition width of about 0.08°K. A peak signal voltage of 0.4 microvolt as against a peak noise level of 0.025 microvolt, SNR = 16, was obtained with this bolometer when $T_1 = 373°$K., $T_2 = 300°$K., $A_1 = 0.39$ cm.^{2}, $d = 60.8$ cm., and $t = 0.001$ sec. The sensitive area of the bolometer, neglecting the solder-covered ends, is 0.008 cm.^{2} For the oxidized iron surface α_1 is taken as 0.79, and α_2 for the aluminum surface as 0.10. Integration of the radiation curves, assuming rock salt transparency below 15 μ and opaqueness above 15 μ to be complete, gives $\beta_1 = 0.70$ and $\beta_2 = 0.56$. Substituting and solving yields

$$Q/t = 0.159 \text{ erg sec.}^{-1}$$

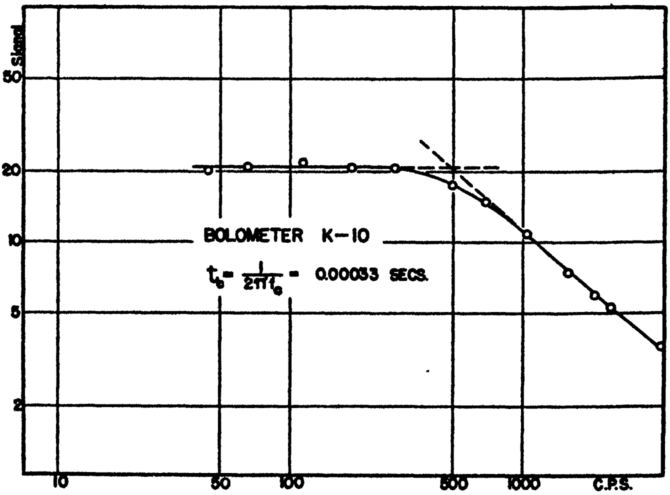

FIG. 9. Response of bolometer K-10 to sine-wave radiation input as a function of frequency.

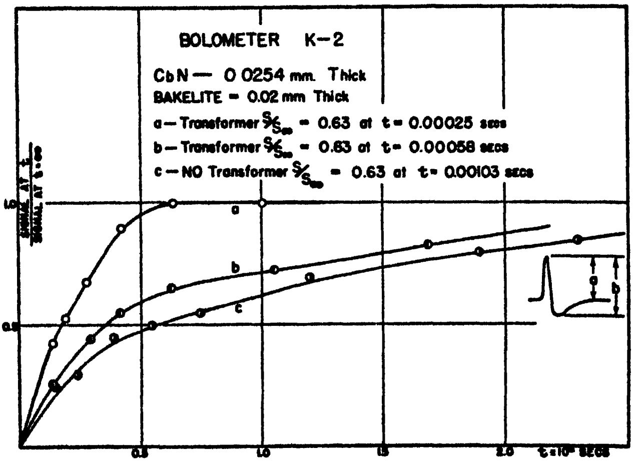

FIG. 10. Response of bolometer K-2 to square-wave input as a function of duration of flash.

Thus the minimum detectable signal, SNR = 1, is for a flux of 1×10^{-2} ergs sec.$^{-1}$ Figure 8 shows the response of this bolometer to the square pulse. The shortest duration pulse tested was for 1.2×10^{-4} sec. At this point the signal is down 48 per cent from the value at 1×10^{-3} sec., so that for a flash of 1.2 ×

10^{-4} sec. the minimum detectable flux is 1.92×10^{-2} ergs sec.$^{-1}$ The energy in this pulse is 2.3×10^{-8} ergs.

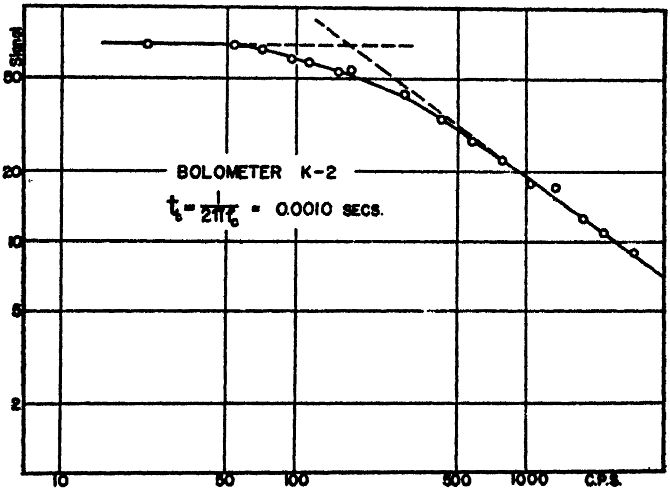

FIG. 11. Response of bolometer K-2 to sine-wave radiation input as a function of frequency.

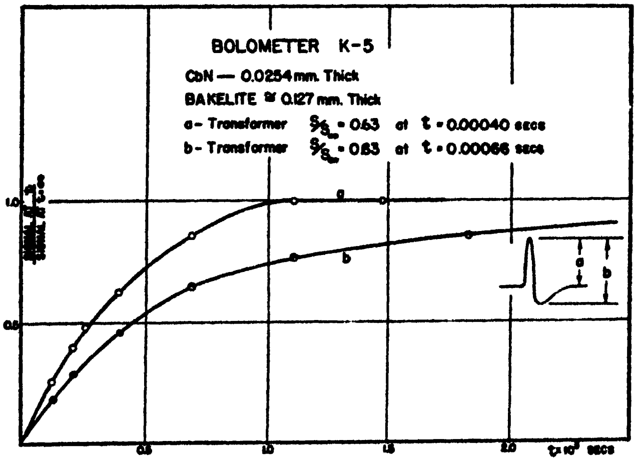

FIG. 12. Response of bolometer K-5 to square-wave input as a function of duration of flash.

Figures 8, 10, and 12 for bolometers K-10, K-2, and K-5, respectively, show the bolometer response to the square-wave input as a function of duration of flash. Figures 9, 11, and 13 show the responses for the same bolometers to sine-wave radiation input. In the latter case either the transformer has been removed or the signal corrected for the attenuation of the transformer, so that the signal is a direct measure of the temperature oscillation. In the square-wave plots, three curves appear. The one taken without the transformer represents the temperature change accurately. Two are taken with the transformer in. One of these is a measure only of that portion of the signal above the center line, while the second is a measure of the total amplitude. It is only the former that is sharp like the radiation wave, and since it is directly proportional to the intensity of radiation and current in the bolometer, it is only the signal and noise above the mean line that are used in sensitivity measurements.

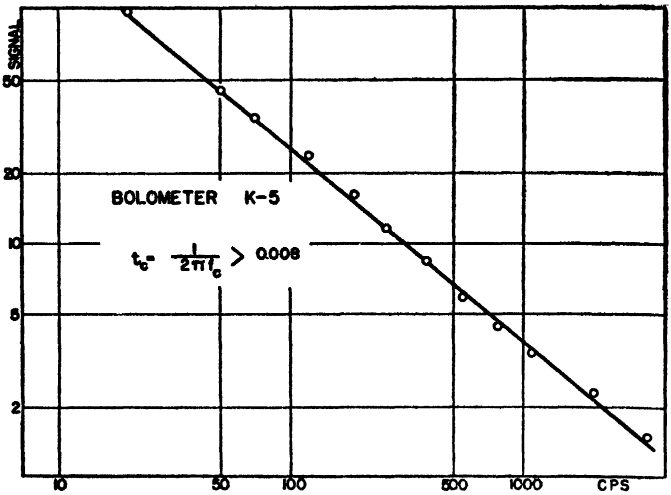

FIG. 13. Response to bolometer K-5 to sine-wave radiation input as a function of frequency.

VI. DISCUSSION OF RESULTS

It is seen that the response curves look very similar to those that would be expected for the simple heat theory predicated earlier. The response times from sine-wave studies agree with those from the square-wave plot when the transformer is not used. The slopes of the high-frequency asymptotes are not -1 but nearer $-\frac{3}{4}$. This is a measure undoubtedly of the deviation from the simple assumptions. The reaction to a square wave when the transformer is in the circuit is such as to give an effective time constant considerably smaller than that determined with sine-wave inputs. Bolometer K-10 has an effective time constant of 1.8×10^{-4} sec. The figures show that by increasing the thickness of bakelite the time constant is increased, and by decreasing the columbium nitride thickness the time constant is decreased.

The heat capacity of columbium nitride has been measured at room temperature (13). If this heat can be broken down into heats of a columbium atomic lattice and a nitrogen atomic lattice, as done in this article, it is possible to assign Debye θ values to each if the relative contributions at room temperature are known. The authors give evidence to support their division of the heats between the two lattices. If their division is used, the Debye θ for columbium is approximately 330 and that for nitrogen 810. This value for columbium falls halfway between those on either side of it in the Periodic Table. On this basis the heat capacity of columbium nitride at 15°K. is 0.19 joules deg.$^{-1}$ gram-mole.$^{-1}$ For the sensitive portion of a superconducting element 0.0254 mm. thick with a density of 8.4, the capacity is 3 ergs deg.$^{-1}$

No measurements have been made on the thermal conductivity of columbium nitride. The electrical resistance is almost constant between 300°K. and 15°K., so if the Wiedemann–Franz law held accurately the thermal conductivity should fall by a factor of 20 in going to 15°K. If we assume that $k = 0.5$ watt cm.$^{-1}$ deg.$^{-1}$ at 300°K., it would be approximately 2.5×10^{-2} watt cm.$^{-1}$ deg.$^{-1}$ at 15°K. The conductivity from the upper surface of the columbium nitride element to the lower would be 8×10^{6} ergs sec.$^{-1}$ deg.$^{-1}$

The value for the thermal conductivity of bakelite lacquer has been placed in the region of 5×10^{-6} watts cm.$^{-1}$ deg.$^{-1}$ at 15°K. by measurements made in this laboratory (7). The thermal conductivity of the bakelite directly beneath the sensitive element and 0.0254 mm. thick would be 1.6×10^{3} ergs sec.$^{-1}$ deg.$^{-1}$

The thermal conductivity of copper at 15°K. is 59.52 watts cm.$^{-1}$ deg.$^{-1}$ (6), and the heat capacity is 0.041 cal. deg.$^{-1}$ mole^{-1} (9). The cross-sectional area of the copper bar of length 26.8 cm. connecting the bolometer base with the hydrogen pot is 0.24 cm.^{2} The heat conductivity of this path is 5.3×10^{6} ergs sec.$^{-1}$ deg.$^{-1}$

Thus in comparing these three thermal conductivities it is seen that there is some justification for neglecting temperature gradients in the columbium nitride, assuming that the copper base is essentially the temperature sink, and placing the important thermal resistance in the bakelite.

There is no good way to estimate the heat capacity of bakelite at 15°K. If, however, the thermal capacity of the bakelite directly between the columbium nitride and the copper base is small with respect to that of the element, we can neglect it and estimate the time constant as

$$t_e = \frac{c}{k} = \frac{3}{1.6 \times 10^{3}} = 0.002 \text{ sec.}$$

VII. NOISE LEVELS

The thermal fluctuations of conduction electrons produce a fluctuating voltage E across a resistance R according to the equation

$$\overline{E^2} = 4kTR\Delta f \tag{8}$$

where T is the absolute temperature and Δf the band width. For a bolometer that in its transition has $R = 1$ used in conjunction with a band pass amplifier of 5000 c.p.s.

$$E = 2 \times 10^{-9} \text{ v.r.m.s.}$$

The measured total noise level of the bolometer, transformer, and amplifier when the bolometer has current passing through it but is either completely normal or superconducting is 1.5×10^{-8} v.r.m.s., calculated at the bolometer level.

This value is the same whether the bolometer is in the circuit or not, showing, as indicated by the above calculation, that the noise level thus observed lies in the transformer or the first tube.

There is a second type of noise that must be considered. If we have a subsystem of thermal capacity C_v that is in equilibrium with a temperature sink, it can be shown that there are statistical fluctuations of the actual energy from the mean value of the energy of the subsystem (8 or 12). The same is true for the temperature of the subsystem and the equations for these fluctuations are

$$\overline{(E - \bar{E}_0)^2} = C_v kT^2 \tag{9}$$

$$\overline{(T - \bar{T}_0)^2} = \frac{kT^2}{C_v} \tag{10}$$

where k is the Boltzmann constant and $\bar{E}_0$ and $\bar{T}_0$ are the mean values of the energy and temperature of the subsystem.

A calculation of these fluctuations for the bolometer with $C_v = 3$ ergs deg.$^{-1}$ gives root-mean-square fluctuations of:

$$\Delta E = 3 \times 10^{-7} \text{ ergs}$$

$$\Delta T = 1 \times 10^{-7} \text{ degree}$$

Since we cannot be sure of the energy to better than 3×10^{-7} ergs, we might not expect to be able to detect energies smaller than this with the present model bolometer. However, with radiation signals that have definite frequency characteristics and with an amplifier passing only a limited band, as in the present case, the interfering temperature fluctuations should be considerably reduced and one should expect to have a limit of detection smaller than 3×10^{-7} ergs. The limit of detection at the present stage of development is 2.3×10^{-6} ergs. Even considering the fact that only a portion of this is absorbed by the detector, it appears to be considerably larger than the limit imposed by statistical fluctuations.

One asks whether this type of noise has ever been observed. As previously mentioned fairly large currents, 0.100 ampere, can be passed through the bolometer when it is completely normal or superconducting without raising the noise level above that from the first tube and transformer. If the columbium nitride has its temperature adjusted so that it is in the steep portion of its transition, the noise will increase. This increased noise is roughly proportional to the current passing through the bolometer and appears to have a random frequency distribution. This type of noise was not observed in the earlier work on this development but only appeared when bolometers approached sensitivities of the order 10^{-5} to 10^{-6} ergs. Thus it has many of the characteristics one would expect of the statistical type of fluctuation we have discussed. In ordinary operation the current in the bolometer was kept such that this noise was just appearing and the peak-to-peak voltage of the noise was 5×10^{-8} volts.

In some bolometers another type of noise was noted. This appeared whether current was passing through the bolometer or not, and only when the element was in a certain portion of its superconducting transition. It consisted of many short-duration 10^{-4} sec. pulses with peak voltages of 0.15×10^{-6} volts.

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THE ENTROPIES AND RELATED PROPERTIES OF BRANCHED PARAFFIN HYDROCARBONS[1,2]

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The status of the data on the entropies of branched paraffin hydrocarbons is reviewed. Experimental values come largely from low-temperature heat-capacity measurements calculated on the basis of the Third Law of Thermodynamics.

Entropy values calculated from statistical formulas and from semistatistical–semiempirical formulas are compared with experimental values. Revisions are made in the statistical formulas in view of recent spectral and other data.

For the branched-chain butane, pentanes, and hexanes, the revised statistical formulas are used to calculate values of the entropy, heat content, free-energy function, and heat capacity of the ideal gases over a range of temperatures.

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I. INTRODUCTION

The thermodynamic properties of paraffin hydrocarbons are of considerable importance for a variety of reasons. The isomers with branched chains, which received less attention in early work, have recently become of greater interest for practical fuels and have received corresponding attention in the laboratory. The entropy is a quantity of particular interest for chemical equilibrium calculations, and it has been obtained experimentally for certain isomers by low-temperature specific-heat measurements and the Third Law of Thermodynamics. In view of the multitude of branched paraffin isomers of higher molecular weight, simple methods of calculation, even though approximate, are very desirable. For isobutane and neopentane (tri- and tetramethylmethanes) relatively exact statistical mechanical calculations can be made. Revised calculations of this type are given in Section III. The methods for these statistical

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[2] This work was supported by Research Project 44 of the American Petroleum Institute with headquarters at the National Bureau of Standards, Washington, D. C.

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calculations have been discussed fully elsewhere (21, 28) and will not be considered in detail here.

II. NORMAL PARAFFINS

Since the straight-chain or normal paraffins are frequently used as a basis of comparison for branched isomers, the status of the data for them will be mentioned. For methane, ethane, and propane relatively detailed statistical calculations have been made and compared with experimental entropies. For butane, pentane, hexane, and heptane, more approximate statistical methods are used which, however, give reasonably good agreement with the experimental values. Table 1 gives the comparison of entropy values. A more detailed discussion of these calculations and tables of related properties may be found in a recent paper (20).

TABLE 1

Entropies of normal paraffins

PARAFFIN	T	S°		REFERENCES FOR EXPERIMENT
		Calculated (reference 20)	Experimental	
	°K.			
Methane	298.16	44.50	44.3 ± 0.3	(11)
Ethane	298.16	(54.85)	54.85 ± 0.15	(29)
Propane	231.09	(60.46)	60.46 ± 0.1	(12)
n-Butane	272.66	(72.06)	72.05 ± 0.2	(6)
n-Pentane	298.16	83.27	83.13 ± 0.2	(15)
n-Hexane	298.16	92.45	92.87 ± 0.3	(9)
n-Heptane	298.16	101.64	102.32	(3, 18)
	371.5	111 5	111 77 ± 0.3	(18)

III. ISOBUTANE AND NEOPENTANE

These two molecules, which may also be described as trimethylmethane and tetramethylmethane, respectively, have rigid carbon skeletons and highly symmetrical structures. Consequently, relatively detailed analyses are possible. In each case the experimental entropy is available from the work of Aston and collaborators (5, 7), and several rough vibrational assignments have been proposed. Since further spectral studies have been made recently, it is now possible to make much better vibrational assignments. These revised calculations are discussed in the following paragraphs.

Table 2 shows, for isobutane, all the Raman lines observed in the important range below 1500 cm.$^{-1}$ together with the infrared bands. The polarization of Raman lines is also given.

In the degenerate symmetry class E, one very low skeletal bending band is expected and three in the range 800 to 1250 cm.$^{-1}$ which may be classified as one carbon–carbon bond stretching and two methyl group wagging motions. The selection of 371, 921, 965, and 1180 cm.$^{-1}$ is definite, in view of the observations.

The 921 infrared band shows clearly a contour characteristic of this class, while the others are fixed by the Raman polarization data. The higher frequencies in this class include a wagging motion of the C—H group expected near 1300 cm.$^{-1}$ on the basis of results for the series CHX_3. Also, there will be the usual CH_3 symmetrical bending at about 1375 cm.$^{-1}$ and unsymmetrical bending (in this case two modes) near 1460 cm.$^{-1}$

TABLE 2

Spectra of isobutane

RAMAN (4, 15)	INFRARED (1)	ASSIGNMENT
371 (4*b*) *D*		*E*
437 (2) *P*	422 m. 437	A_1
795 (10) *P*	784 799 s. 816	A_1
	913 930 v.s.	*E*
965 (4*b*) *D*		*E*
1098 (1*b*)	1095 w.	A_1
1172 (4*sb*) *D*	1180 v.s.	*E*
	1210 1225 w. 1240	(437 + 795), (A_1)
1322 to (3*b*) *D* 1355	1335 s.	*E*
	1377 v.s.	$E + A_1$
1452 (7*b*) *D*	1475 v.s.	*E* $E + A_1$

The totally symmetric class A_1 (polarized in the Raman) includes a low, skeletal bending frequency, clearly 437 cm.$^{-1}$, and a carbon–carbon stretching motion, 799 cm.$^{-1}$ In addition, there will be one methyl wagging motion somewhere below 1200 cm.$^{-1}$ The 1095 band seems by far the most probable selection, although the band contour is doubtful. The Raman data independently favor this selection. In addition, there must be lines near 1375 and 1460, although these are not separated.

The three vibrations in the remaining symmetry class, A_2, are forbidden in both the Raman and infrared spectra, so they must be assigned on other bases. Fortunately, all modes but one can be readily and reliably estimated. The final uncertain mode in this class is the methyl wagging motion. It would be expected to be in the general range 900–1200 cm.$^{-1}$ The top value, 1200 cm.$^{-1}$, gives best agreement with the specific-heat data for the gas (8) and is adopted for that reason.

Table 3 shows the complete assignment of the vibration frequencies of isobutane.

The moments of inertia were calculated from the dimensions: C—C, 1.54 Å.; C—H, 1.09 Å.; tetrahedral angles. The product of the principal moments is then 2113×10^{-117} (g.cm.^{2})^3. By comparison with the Third Law entropy at the boiling point (5) the barrier to internal rotation was found to be 3620 cal. per mole.

TABLE 3

Vibration frequencies of isobutane

	SKELETAL	C—C STRETCHING	CH_3 WAGGING	CH_3 SYMMETRICAL δ	CH_3 UNSYMMETRICAL δ	CH δ	CH_3 SYMMETRICAL STRETCHING	CH_3 UNSYMMETRICAL STRETCHING	CH STRETCHING	INTERNAL ROTATION	ACTIVITY
A_1	437	799	1098	1377	1460		2950	2950	2950		*IR*, *R*(*p*)
A_2			(1200)		1460			2950		?	i.a.
E	371	921	965	1377	1460	1335	2950	2950		?	*IR*, *R*(*dp*)
			1172		1460			2950			

Table 4 shows, for neopentane, the Raman lines and the important infrared bands, together with their assignments. Table 5 shows the complete vibrational assignment of neopentane.

The two Raman lines at 335 cm.$^{-1}$ and 414 cm.$^{-1}$ are undoubtedly due to the *E* and T_2 skeletal deformation frequencies, respectively. The A_1 and T_2 C—C stretching modes should be well separated, the former below 1000 cm.$^{-1}$ and the latter above, because of the difference in reduced mass involved in the motions. In the A_1 mode, the central carbon does not move and so is effectively an infinite mass. In the T_2 mode, however, a considerable displacement of this carbon atom is to be expected. The frequencies 733 cm.$^{-1}$ and 1250 cm.$^{-1}$ have been assigned, therefore, to the A_1 and T_2 C—C stretching modes.

The infrared band at 925 cm.$^{-1}$ is probably due to T_2 methyl wagging. The other two methyl wagging frequencies do not appear in the spectrum. The one with the symmetry T_1 is forbidden in both infrared and Raman spectra, while the other with the symmetry *E* may appear in the Raman spectrum only. The values 950 and 1150 cm.$^{-1}$ have been estimated for T_1 and *E*, respectively.

The infrared band at 1370 cm.$^{-1}$ has been selected for T_2 symmetric CH_3 bending and 1360 cm.$^{-1}$ estimated for the same motion with the symmetry A_1.

The value 1470 cm.$^{-1}$ has been assigned to E, T_2, and T_1 unsymmetrical methyl bending.

TABLE 4

Spectra of neopentane

RAMAN (24, 25)	INFRARED (2)	ASSIGNMENT
335 (10)		E
414 (3)		T_2
733 (20)		A_1
	$\left.\begin{array}{r}822\\835\end{array}\right\}$ (0)	2 × 414
925 (15B)	$\left.\begin{array}{r}917\\926\\937\end{array}\right\}$ (2)	T_2
	990 (0)	
	1148 (0)	414 + 733
	~1200 (1s)	
1252 (20B)	1257 (9)	T_2
	$\left.\begin{array}{r}1364\\1376\\1385\end{array}\right\}$ (10)	T_2
1455 (15)	$\left.\begin{array}{r}1460\\1475\\1488\end{array}\right\}$ (10)	$E + T_2$

TABLE 5

Vibration frequencies of neopentane

	SKELETAL	C—C STRETCHING	CH_3 WAGGING	CH_3 SYMMETRICAL δ	CH_3 UNSYMMETRICAL δ	CH STRETCHING	INTERNAL ROTATION	ACTIVITY
A_1		733		(1360)		2913		$R(p)$
A_2							?	i.a.
E	335		(1150)		(1470)	(2950)		$R(dp)$
T_2	414	1250	925	1370	1470	(2900, 2950)		IR, $R(dp)$
T_1			(950)		(1470)	(2950)	?	i.a.

The spectral region around 2900 cm.$^{-1}$ is very complicated, as is usual in molecules containing several methyl groups. However, the Raman line at 2913 cm.$^{-1}$ was chosen for the A_1 C—H stretching motion, 2950 cm.$^{-1}$ for the motion with the symmetry E, 2900 and 2950 cm.$^{-1}$ for T_2, and 2950 cm.$^{-1}$ for the inactive T_1 motion.

The four internal rotations combine to give one mode with the symmetry A_2 and one triply degenerate mode of symmetry T_1. Both of these are inactive.

The product of the principal moments was calculated to be 6726×10^{-117} $(\text{g.cm.}^2)^3$. By comparison with the Third Law entropy (7), the barrier to internal rotation was found to be 4300 cal. per mole.

IV. ISOPENTANE AND THE BRANCHED HEXANES

These molecules have internal rotations within their carbon skeletons and are consequently more complex for theoretical treatment. However, we now have available accurate experimental entropies for all except 3-methylpentane. This last substance has never been frozen and hence has not been handled by the Third Law method. The value in table 6 is obtained from the equilibrium with 2-methylpentane (10, 14) and the heat of isomerization (23).

Two approximate methods of calculation will be considered. The first is the very simple, partly empirical formula of Pitzer and Scott (22), which is given in equation 1.

$$S = S_n + R \ln 2 + R \ln (I/\sigma_e \, \sigma_i) - 3.5B \tag{1}$$

S_n is the entropy of the normal isomer and $R \ln 2$ a correction for its symmetry number, I is the number of optical or other isomeric forms included in the structural isomer being considered, σ_e and σ_i are the symmetry numbers for external rotation and for the internal rotation of the carbon skeleton, respectively, and B is the number of chain branchings. The constant 3.5 cal. per degree is an empirical factor for all effects of branching not included in detail. This method will be designated the "simplified" method and is particularly appropriate for still more complex molecules. In the hexanes we are testing its accuracy.

The second method is a modification of the approximate statistical formulas for the n-paraffins (19). Its character is indicated in equation 2.

$$\begin{aligned} S = S_0 &+ N_1\,(\text{C—C stretching}) + N_2\,(\text{C—C bending}) + N_3\,(\text{internal rotation}) \\ &+ S_{\text{steric}} + R \ln I/\sigma_e + N_4(\text{CH}_3) + N_5(\text{CH}_2) + N_6(\text{CH}) + N_7(\text{C}) \\ S_{\text{steric}} &= R(\ln Q + T \, \mathrm{d} \ln Q/\mathrm{d}T) \\ Q &= \sum_i e^{-E_i/RT} \end{aligned} \tag{2}$$

With occasional exceptions all terms are functions of temperature. N_1, N_2, N_3 are the numbers of C—C stretching and bending motions and the number of skeletal internal rotations, respectively. $N_4 \ldots N_7$ are the numbers of CH_3, CH_2, CH, and C groups in the molecule. In the equation for Q the quantity E_i is the steric strain energy of the molecule in a particular configuration. This has been expressed in terms of a parameter a from the n-paraffins whose value is 800 cal. per mole. This formula has been derived and explained elsewhere (19). More recently, revised sets of vibration frequencies have been recommended for the (CH_3) and (CH_2) terms (20). This will be called the "statistical" method.

Table 6 contains a comparison of experimental and calculated entropies for these molecules. The previous calculations contained certain errors in the assignment of steric energies. To be consistent with isopentane and the n-paraffins that for 2-methylpentane should be two positions at 0 energy, two at a, one at $2a$, and four at ∞. Then 3-methylpentane should probably have two positions at 0 energy, one at a, four at $2a$, and two at ∞. The latter set is still rather arbitrary but is more consistent than the previous assignment. 2,3-Dimethylbutane also involves steric positions different from those for simpler molecules and no definite assignment can be made. It clearly consists of one lowest position and two of higher energy. While the previous difference of $2a$ seems somewhat more reasonable structurally, a value of a is needed to fit the experimental entropy closely. The revised values are shown in table 6. While these steric assignments are very unsatisfactory in that they are somewhat subjective, nevertheless the magnitude of error from this source is limited to about 1 cal. per degree.

TABLE 6

The entropies of isopentane and the branched hexanes

Ideal gas state, $T = 298.16°K$.

PARAFFIN	S SIMPLIFIED	S STATISTICAL	S EXPERIMENTAL FROM 14°K.	REFERENCE TO EXPERIMENT
2-Methylbutane	81.2	81.98	82.01 ± 0.55	(27)
2-Methylpentane	90.3	90.65	90.89 ± 0.17	(3,9)*
3-Methylpentane	90.3	90.77	91.0 ± 1.0	
2,2-Dimethylbutane	84.6	85.7	85.55 ± 0.17	(3,9)
			85.72 ± 0.2	(13)
2,3-Dimethylbutane	85.4	87.30	87.39 ± 0.17	(3,9)

* The references (3,9) indicate the entropy of the liquid from reference 9 with vaporization data from reference 3.

Fortunately 2,2-dimethylbutane has only a single type of steric position, so that no uncertainty arises from that source. Equation 2 gives essentially exact agreement with the experimental value in this case. A more detailed statistical treatment has also been published for 2,2-dimethylbutane (13) in which potential barriers are adjusted to fit the entropy. Values from this source are included in Section VI.

V. BRANCHED HEPTANES AND OCTANES

In the range of paraffins heavier than the hexanes the experimental data are fragmentary. Parks and collaborators (17) have measured by the Third Law method the entropies of most of the heptanes and of a few octanes. Their experimental measurements are reliable but extend only down to 90°K., which leaves a very large extrapolation to 0°K. While this extrapolation appears to have been about correct for the normal paraffins, in the case of 2,2,4-trimethylpentane it is too small by over 3 cal. per degree. Thus the entropy values based on measurements only to 90°K. (see table 7) are probably from one to four units too small and in any case subject to considerable uncertainty. For two trimethylpentanes we have accurate Third Law values (based on measurement to 14°K.).

TABLE 7

The entropies of branched heptanes and octanes

Ideal gas state, $T = 298.16$°K.

	S° SIMPLIFIED (22)	S° STATISTICAL (19)	S° EXPERIMENTAL FROM 14°K. (18, 22)	EXPERIMENTAL FROM 90°K. (17)
Heptanes:				
2-Methylhexane	99.4	99.5		98.4
3-Methylhexane	100.8	101.3		
3-Ethylpentane	97.2	98.3		97.7
2,2-Dimethylpentane	93.7	93.4		90.2
2,3-Dimethylpentane	97.3	98.8		
2,4-Dimethylpentane	94.5	94.7		92.0
3,3-Dimethylpentane	94.5	95.4		92.2
2,2,3-Trimethylbutane	90.2	92.3		86.5
Octanes:				
2-Methylheptane	108.5	108.6		
3-Methylheptane	109.9	110.1		
4-Methylheptane	108.5	108.1		
3-Ethylhexane	108.5	109.3		
2,2-Dimethylhexane	102.8	102.9		
2,3-Dimethylhexane	106.4	105.9		
2,4-Dimethylhexane	106.4	106.3		
2,5-Dimethylhexane	103.6	104.7		
3,3-Dimethylhexane	105.0	104.5		
3,4-Dimethylhexane (meso)	105.0	105.5		
3,4-Dimethylhexane (*dl*)	105.0	104.2		
2-Methyl-3-ethylpentane	105.0	105.2		
3-Methyl-3-ethylpentane	102.8	103.3		
2,2,3-Trimethylpentane	100.7	101.4		
2,2,4-Trimethylpentane	99.3	101.4	101.15	97.95
2,3,4-Trimethylpentane	101.5	102.8	102.31	
2,3,3-Trimethylpentane	101.5	102.9		
2,2,3,3-Tetramethylbutane	92.3	94.1		88.6

Calculated values are available from both the "simplified" and the "statistical" formulas. The "statistical" calculations are subject to the same revisions of vibration frequencies and steric energies which were made for the hexanes. However, the changes would be well within the uncertainty which must be allowed until further experimental values are obtained. Consequently, it seems hardly worthwhile to repeat the calculations now. (For 2-methylhexane there was a small but definite error previously; this is corected.)

TABLE 8

Heat capacity, C_p°

Units: calories per degree mole

T	*n*-BUTANE	ISO-BUTANE	*n*-PENTANE	2-METHYL-BUTANE	2,2-DI-METHYL-PROPANE	*n*-HEXANE	2-METHYL-PENTANE	3-METHYL-PENTANE	2,2-DI-METHYL-BUTANE	2,3-DI-METHYL-BUTANE
°*K.*										
298.16	23.61	23.14	29.30	28.83	29.07	35.06	34.46	35.14	34.25	34.64
300	23.77	23.25	29.51	28.97	29.21	35.32	34.63	35.31	34.43	34.84
400	29.80	29.77	36.91	37.05	37.55	44.04	44.0	44.6	44.2	44.3
500	33.54	35.62	43.96	44.23	45.00	52.39	52.5	52.9	53.0	52.8
600	40.42	40.62	49.88	50.28	51.21	59.38	59.6	59.9	60.4	60.0
700	44.61	44.85	54.98	55.41	56.40	65.35	65.7	65.9	66.5	65.9
800	48.23	48.89	59.37	59.80	60.78	70.51	70.8	71.0	71.7	71.1
900	51.42	51.65	63.21	63.60	64.55	75.01	75.3	75.4	75.9	75.5
1000	54.20	54.40	66.57	66.90	67.80	78.94	79.2	79.3	79.9	79.4
1100	56.60	56.81	69.46	69.80	70.62	82.32				
1200	58.72	58.89	72.01	72.29	73.04	85.30				
1300	60.55	60.71	74.22	74.47	75.15	87.89				
1400	62.15	62.29	76.14	76.37	76.99	90.12				
1500	63.51	63.67	77.76	78.01	78.60	92.02				

TABLE 9

Entropy, S^0

Units: calories per degree mole

T	*n*-BUTANE	ISO-BUTANE	*n*-PENTANE	2-METHYL-BUTANE	2,2-DI-METHYL-PROPANE	*n*-HEXANE	2-METHYL-PENTANE	3-METHYL-PENTANE	2,2-DI-METHYL-BUTANE	2,3-DI-METHYL-BUTANE
°*K.*										
298.16	74.10	70.42	83.27	81.98	73.23	92.45	90.65	90.77	85.72	87.33
300	74.25	70.55	83.44	82.15	73.40	92.67	90.88	91.00	85.92	87.53
400	81.91	78.13	92.95	91.58	83.00	104.03	102.1	102.4	97.2	98.8
500	89.20	85.45	101.94	100.65	92.17	114.75	112.9	113.3	108.1	109.7
600	96.11	92.40	110.48	109.23	100.94	124.91	123.1	123.6	118.4	120.0
700	102.66	98.98	118.56	117.40	109.23	134.52	132.7	133.3	128.1	129.7
800	108.87	105.21	126.19	125.11	117.07	143.60	141.9	142.4	137.4	138.8
900	114.74	111.11	133.41	132.37	124.45	152.16	150.5	151.0	146.0	147.4
1000	120.31	116.69	140.26	139.24	131.41	160.29	158.6	159.2	154.3	155.6
1100	125.59	121.99	146.74	145.76	138.00	167.97				
1200	130.60	127.03	152.89	151.95	144.26	175.27				
1300	135.37	131.82	158.74	157.82	150.20	182.20				
1400	139.91	136.37	164.31	163.41	155.84	188.79				
1500	144.22	140.67	169.60	168.67	161.19	195.03				

It may be noted from tables 6 and 7 that the statistical method gives values within a few tenths of a calorie per degree of all reliable experimental values (from 14°K.). However, in other cases the uncertainty should still be taken as 1 cal. per degree. We believe that this is considerably less than the uncertainty

TABLE 10

The heat-content function, $(H^0 - H_0^0)/T$

Units: calories per degree mole

T	*n*-BUTANE	ISOBUTANE	*n*-PENTANE	2-METHYL-BUTANE	2, 2-DI-METHYL-PROPANE	*n*-HEXANE	2-METHYL-PENTANE	3-METHYL-PENTANE	2, 2-DI-METHYL-BUTANE	2, 3-DI-METHYL-BUTANE
°K.										
298.16	15.58	14.34	19.01	17.24	16.87	22.44	20.45	20.62	19.91	20.36
300	15.63	14.39	19.07	17.31	16.94	22.52	20.54	20.71	19.99	20.45
400	18.42	17.41	22.62	21.23	21.07	26.83	25.2	25.5	24.9	25.2
500	21.27	20.50	26.18	25.13	25.13	31.10	29.9	30.2	29.6	29.9
600	24.06	23.45	29.64	28.83	28.98	35.23	34.2	34.6	34.2	34.4
700	26.71	26.20	32.90	32.27	32.53	39.11	39.3	38.6	38.3	38.4
800	29.18	28.76	35.93	35.44	35.80	42.71	42.0	42.4	42.2	42.2
900	31.46	31.13	38.73	38.36	38.78	46.02	45.5	45.8	45.6	45.7
1000	33.58	33.31	41.34	41.03	41.51	49.11	48.7	48.9	48.9	48.8
1100	35.56	35.34	43.76	43.52	44.02	51.97				
1200	37.40	37.23	46.01	45.83	46.34	54.63				
1300	39.12	38.96	48.10	47.94	48.49	57.10				
1400	40.71	40.56	50.04	49.90	50.47	59.39				
1500	42.18	42.03	51.84	51.69	52.28	61.50				
ΔH_0^0 (calories per mole)	−23,332	−24,602	−27,270	−28,660	−31,300	−30,980	−32,080	−31,490	−34,610	−32,880

TABLE 11

The free-energy function, $-(F^0 - H^0_0)/T$

Units: calories per degree mole

T	*n*-BUTANE	ISOBUTANE	*n*-PENTANE	2-METHYL-BUTANE	2, 2-DI-METHYL-PROPANE	*n*-HEXANE	2-METHYL-PENTANE	3-METHYL-PENTANE	2, 2-DI-METHYL BUTANE	2, 3-DI-METHYL-BUTANE
°K.										
298.16	58.52	56.08	64.26	64.74	56.36	70.01	70.20	70.15	65.81	66.97
300	58.62	56.16	64.37	64.84	56.46	70.15	70.34	70.29	65.93	67.08
400	63.49	60.72	70.33	70.35	61.93	77.20	76.9	76.9	72.4	73.6
500	67.93	64.95	75.76	75.52	67.04	83.65	83.0	83.1	78.4	79.8
600	72.05	68.95	80.84	80.40	71.96	89.68	88.8	89.0	84.2	85.7
700	75.95	72.78	85.66	85.13	76.70	95.41	94.4	94.6	89.8	91.2
800	79.69	76.45	90.26	89.67	81.27	100.89	99.8	100.1	95.2	96.6
900	83.28	79.98	94.68	94.01	85.67	106.14	105.0	105.3	100.4	101.8
1000	86.73	83.38	98.92	98.21	89.90	111.18	110.0	110.3	105.4	106.8
1100	90.03	86.65	102.98	102.24	93.98	116.00	114.7	115.1	110.2	111.6
1200	93.20	89.80	106.88	106.12	97.92	120.64	119.3	119.7	114.8	116.0
1300	96.25	92.86	110.64	109.88	101.71	125.10	123.8	124.2	119.3	120.6
1400	99.20	95.81	114.27	113.51	105.37	129.40	129.1	128.5	123.6	125.0
1500	102.04	98.64	117.76	116.98	108.91	133.53	132.2	132.6	127.8	129.1
ΔH_f (calories per mole). .	−23,332	−24,602	−27,270	−28,660	−31,300	−30,980	−32,080	−31,490	−34,610	−32,880

in the extrapolation of the heat capacity below 90°K.; hence, the statistical values are recommended as more reliable than values based on experimental measurements from 90°K. Values from the simplified formula are naturally less accurate but are within 2 cal. per degree. This formula should give useful estimates for nonanes, decanes, etc.

VI. CALCULATED THERMODYNAMIC FUNCTIONS

In Sections III and IV, previous statistical entropy calculations for the branched butane, pentanes, and hexanes have been revised to take account of recent data. Several thermodynamic functions may be calculated by these same statistical methods. Values of these functions for a range of temperatures are presented in tables 8 to 11. Also included are values for the *n*-paraffins for comparison (20). As discussed above, the detailed statistical method was used for isobutane, neopentane, and neohexane (2,2-dimethylbutane). The approximate statistical method of equation 2 was used for isopentane and the remaining branched hexanes.

Values of ΔH_0^0 calculated from heat of formation data (23) are included for convenience in calculations.

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FIVE YEARS OF APPLIED SCIENCE IN THE LOW-TEMPERATURE FIELD[1]

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For a five-year period ending in 1945 a large fraction of the M.I.T. group interested in low-temperature research turned to the development of compact light-weight oxygen-producing units based on distillation of liquefied air. The units were designed for the special purposes of the armed services: gaseous oxygen for respiratory use, for welding and cutting, and liquid oxygen for other requirements. The last units designed produced liquid oxygen and high-pressure gaseous oxygen as desired, but the development was interrupted upon cessation of hostilities. The model units built in the Institute shops are described, and also the units manufactured on the basis of the models. Attention is called to important gaps in published scientific information needed for the rational design of gas-liquefying apparatus and devices for the separation of constituents by distillation.

I. INTRODUCTION

The first project discussed in the summer of 1940 was that of the large-scale production of liquid oxygen on board submarines, amounting to from 1000 lb. to 5000 lb. per hour. The equipment was to be placed in a submarine space measuring 382.5 cu. ft., and the total weight was not to exceed 275,000 lb. The means suggested by the group at the Massachusetts Institute of Technology involved the use of turbo compressors and expanders, but no facilities existed therefor beginning such a development. Indeed, we had no knowledge of a turbine expander having been designed in the United States, but large-capacity turbocompressors had been developed in Europe. According to estimates, even if the turbo equipment were available, the submarine space allotted for the equipment (382.5 cu. ft.) was too small for the production of 1000 lb. per hour of liquid oxygen.

The basis of experience available to the M. I. T. Oxygen Group lay in the design and operation over many years of laboratory liquefaction systems principally for air and hydrogen. During the two years preceding 1940, however, considerable time had been given by Dr. Samuel C. Collins to the design and operation of expansion engines. Out of this effort there came, among other developments, a diaphragm expander tested considerably in a helium circuit producing temperatures of 10°K. and directed at the time to the production of liquid helium without the use of liquid hydrogen or liquid air. The experience led to the development and construction by Dr. Collins—under the oxygen program—of the reciprocating gas-lubricated expansion engine, later manufactured by Clark Brothers at Olean, New York.

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[1] Presented at the Symposium on Low-Temperature Research which was held under the auspices of the Division of Physical and Inorganic Chemistry at the 109th Meeting of the American Chemical Society, Atlantic City, New Jersey, April, 1946.

[2] The work of the project was carried out by the following associates: Samuel C. Collins—October 1940 to July 1942; Howard O. McMahon—October 1940 to September 1942, Robert P. Cavileer—October 1940 to May 1945; Kendall C. Valentine—October 1940 to August 1942; James A. Beattie—June and July 1941; James L. Hildebrand—January 1941 to October 1942; Charles L. Gallagher—July 1941 to March 1945; Knut W. Wilhelmson—July 1941 to June 30, 1945; Clark C. Stephenson—February 1942 to June 1942; Dudley A. Williams—April 1942 to June 30, 1945; Thomas E. White—July 1942 to May 1945; Charles E. Teeter, Jr.—August 1942 to February 1945; Norman B. Carter—April 1943 to June 30, 1945.

Prior to embarking on the oxygen program for the National Defense Research Committee, the members of the laboratory interested in low-temperature research had devoted considerable discussion to the advantage of a novel compressor employing no liquid lubrication, suggested by Dr. Collins. There had also been emphasized the need of efficient heat interchangers in low-temperature maintenance, an emphasis which led to a considerable testing program for different types of construction several years prior to 1940. The developments were continued under the N. D. R. C. contract but on an extended scale.

During the autumn of 1940 and throughout the following winter the problem of a liquid-air rectifier for the production of oxygen aboard vessels or airplanes was considered, and a number of designs were tested. A satisfactory solution of the problem meeting the restricting conditions proved difficult of attainment, and work was still in progress in the fall and winter of 1941–42. A successful application of Dr. McMahon's work on rotating columns was embodied, however, in the final oxygen producer completed by Dr. Collins and Dr. McMahon. A further application of the rotating column for shipboard use with modifications is represented by the high-pressure oxygen gas–liquid oxygen unit completed in the spring of 1944.

The first model of the airplane unit of Collins and McMahon was shipped to Dayton, Ohio, for test in the interest of the Wright Field Air Force group in September 1942. The further development and perfection of the unit by Drs. Collins and McMahon took place at the plant of the Frigidaire Company at Dayton. Numerous examples of the Collins–McMahon unit embodying Dr. Collins' special interchanger clean-up system for water and carbon dioxide were manufactured commercially for the Armed Services.

Request for a unit for replenishing the respiratory oxygen on submarines was made in the late summer of 1942 and led to the design of a compact high-pressure unit to operate with or without precooling. The unit was to be supplied with air feed from either of the two submarine compressors normally used to charge air into the air flasks of torpedoes. The normal capacity of the submarine compressors is 300 lb. of air per hour at 3000 p.s.i. The yield of oxygen obtainable without precooling is 20 lb. per hour of liquid oxygen, and 35 lb. per hour with precooling to −40°C. Purity ranges were from 0.985 to 0.99 mole fraction (m.f.) or better. The model unit was tested and inspected at the Engineering Laboratory of the U. S. Naval Academy at Annapolis, Maryland. Four examples of the unit were later made by Servel Inc., two of which were sent to England.

In February 1943 the request was made on the part of the Bureau of Ships of the U. S. Navy for the development of a dual-purpose oxygen-producing unit to produce liquid oxygen without and with precooling, and also to produce high-pressure oxygen gas directly. Since the unit was to be used on supply ships it was necessary to provide a rotating column. The unit was to be adapted for air feed in amounts of 120 cu. ft. per minute (c.f.m.) at 3000 p.s.i., or 540 lb. per hour. The purity of the oxygen was to be 99.5 per cent; the quantity of oxygen obtainable was to be not less than 70 lb. per hour.

A unit of the above description will produce the maximum amount of liquid oxygen when fed with precooled air (-45° to 50°C.) at the full 3000 p.s.i. For the production of gaseous oxygen at 2000 p.s.i. pressure, however, a much lower pressure of the air feed is required (1500 p.s.i. roughly) with no precooling, since the conversion of the liquid oxygen into gas in the interchanger provides ample refrigeration for the production of the maximum amount of oxygen consistent with the use of a simple stripping rectifier.[3]

In order to realize the type of unit suggested it was necessary to produce a liquid-oxygen injection pump which would take liquid from the boiler of the rectifier, raise it to 2000 p.s.i. or more, and inject it into the main heat interchanger. The pump evolved operates or is driven by air pressure supplied by a branch line from the air feed, the cool exhaust therefrom being introduced into the low-pressure channel of the interchanger at the appropriate temperature.

Photographs of the model units constructed at M. I. T. are reproduced and also of units manufactured on the basis of the models by Servel Inc. at Evansville, Indiana, and the Independent Engineering Company at O'Fallon, Illinois. Several of the earlier types of interchangers (3, 5) were also retested. Several new types were, however, brought to a perfected state of development, notably the edge-wound copper-ribbon-packed interchanger devised by Dr. Collins, which contributed so largely to the satisfactory clean-up performance of his alternating channel feed effluent heat interchanger, whereby in low-pressure units cargon dioxide, oil vapors, and water vapor are completely removed.

II. THE COLLINS McMAHON AIRPLANE UNIT

Early in the program (spring 1940) the National Defense Research Committee brought to the attention of the group information pertaining to the development of a high-pressure oxygen unit at the Mond Laboratory of the University of Cambridge, England. The work had been undertaken on the request of the British Air Services for an air-borne oxygen-producing unit to supply respiratory oxygen. The Mond model unit was received at M. I. T. and tests were conducted after some minor substitutions of parts and adjustments, together with the construction of a solid potassium hydroxide remover for carbon dioxide and an alumina dehydrator. The unit produced 8.5 lb. per hour of gaseous oxygen of 0.95 m.f. purity. Meanwhile, and prior to the receipt of the Mond model unit, the airplane unit referred to above had been designed and executed by Dr. Collins and Dr. McMahon, tests upon which were reported in September 1942.

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[3] It is established commercial practice with certain systems to use precooling in the production of gaseous oxygen at low pressure. Similarly precooling could be used with the unit described above in producing high-pressure gas, thereby bringing about a substantial further reduction of the pressure of the air feed.

This unit weighed a total of 320 lb. complete, exclusive of the compressor.[4] Among other novel features, the unit was provided with the edge-wound copper-ribbon-packed interchanger channels and the gas-lubricated piston expander (weight complete, 46.5 lb.). The rotating column was designed and built by Dr. McMahon for the unit on the basis of his work on rotating columns begun early in the program. The complete column weighed but 19.5 lb. The unit operated with air feed at 150 p.s.i.a. in the amount of 1500 cu. ft. per hour (c.f.h.) or 25 cu. ft. per minute (c.f.m.). Production of gaseous oxygen proved to be: 200 c.f.h. of purity 0.97 m.f.; 150 c.f.h. of purity 0.99 m.f.; 110 c.f.h. of purity 0.995 m.f. The starting time from the warm condition was 2 hr.; if the unit had been operated the previous day, 1 hr.[5]

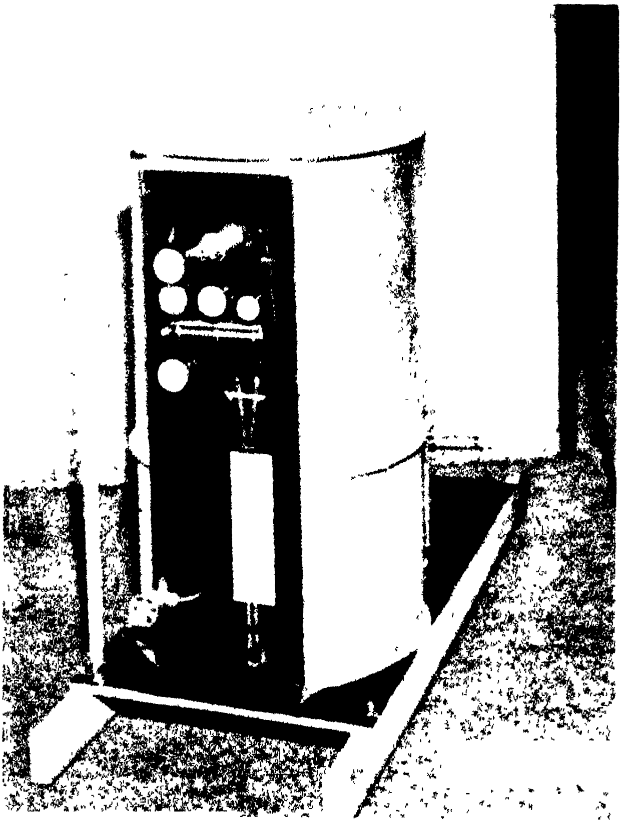

FIG. 1 Front view of Collins-McMahon airplane unit (M. I. T. model)

Figure 1 shows the front view of the instrument and control panel view of the Collins-McMahon model airplane unit as it was being prepared for shipment. Figure 2 is the rear view, showing the expander valve timing gears and exchanger alternating channel shift timing. Figure 3 gives an impression of the unit with case and insulation removed, viewed from the timing-gear side. The gas-lubricated expansion-engine cylinder in the foreground is mounted directly on the cross-head unit, while the column is surrounded by the heat interchanger.

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[4] The insulation used in the model unit was of greater density than desirable and added considerable weight over that realized later when glass wool was employed The insulation, of course, had to be incombustible.

[5] Later, when insulating material of less density was used, the starting time was reduced.

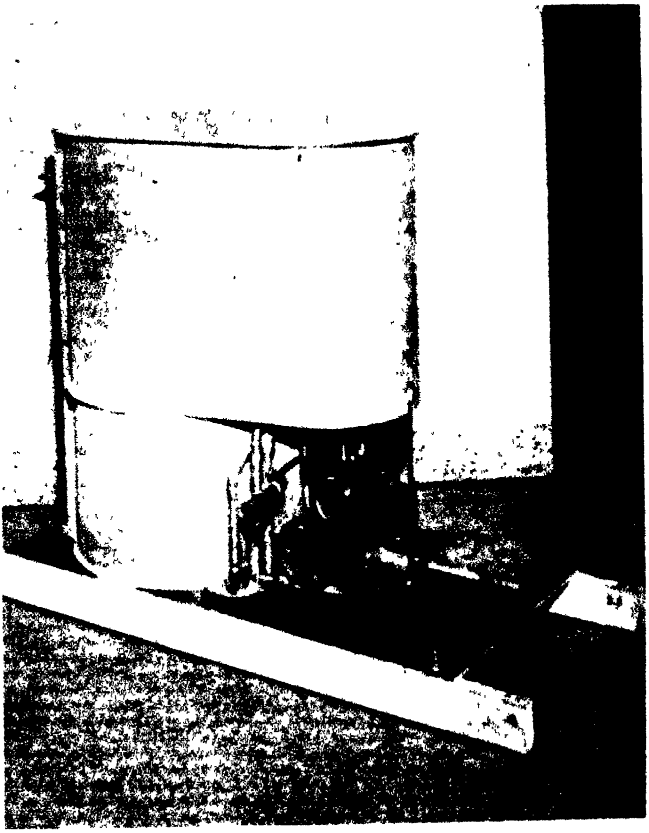

FIG. 2. Rear view of Collins-McMahon airplane unit (M. I. T. model), showing engine

Figure 4 gives a view of the gear side, the opposite side from that represented in figure 3.

III. THE SUBMARINE LIQUID-OXYGEN PRODUCER

The replenishment of respiratory oxygen in submerged submarines was discussed in the spring of 1942. The plan was to use the torpedo compressors to supply the air for the oxygen producer. The space available for the unit was a floor area not to exceed 4 sq. ft. and a height of 6 ft. Another requirement was that the unit should start producing liquid oxygen in the shortest possible time, since production would be limited to relatively short intervals when the vessel was at ocean surface. The unit was also to require practically no attention during operation.

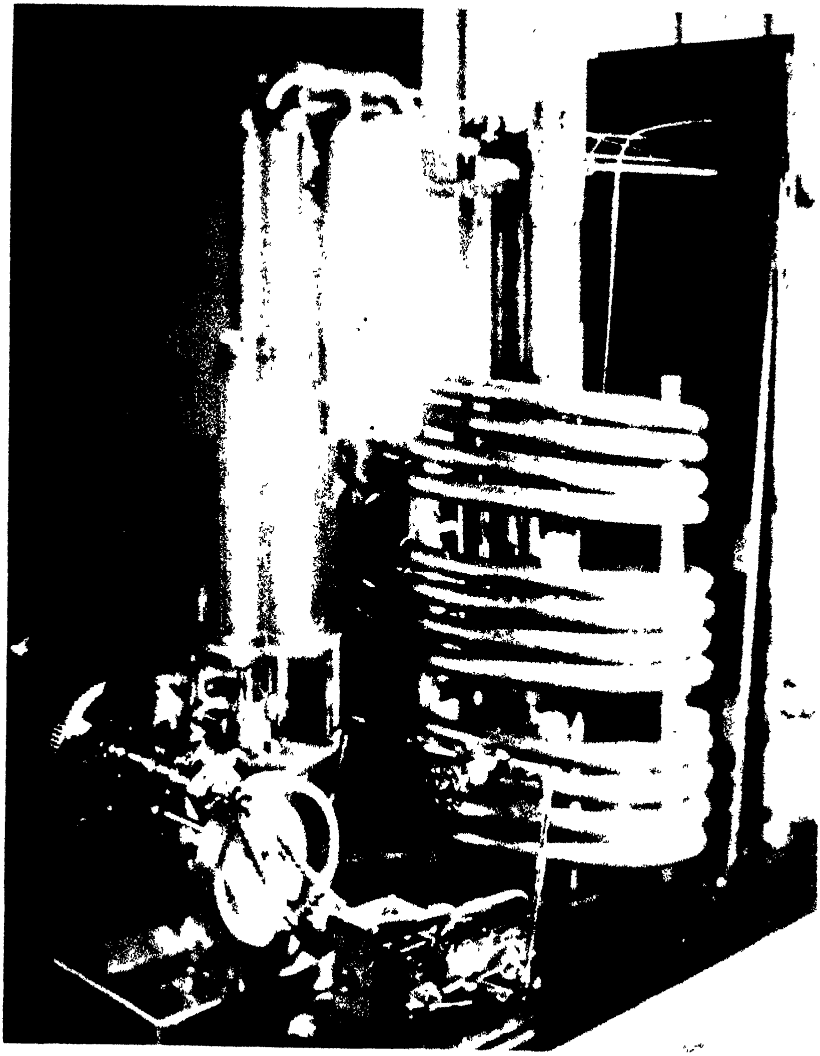

FIG. 3. Collins-McMahon airplane unit (M. I. T. model) with case and insulation removed; timing-gear side

The submarine unit as designed and constructed at M. I. T. was cylindrical in shape, 18 in. in diameter and 50 in. in height (figure 5). All instruments were on the top surface, as were also all connections for entrance and exit of fluids (figure 6). Ordinarily a U-shaped liquid-oxygen level indicator is used in commercial practice. The requirement in the present instance was a level indicator which would not be deranged when the unit was inverted or laid upon its side, as would be likely to occur in introducing the unit through the submarine hatch or in the course of installation. Accordingly, a sensitive-diaphragm gauge mechanism was made use of in a hermetically sealed case. The liquid level of the boiler case was used for the connection to the gauge case, and the floor of the liquid-oxygen chamber for the connection to the gauge diaphragm to which the translating mechanism and indicating needle of the gauge were attached. The

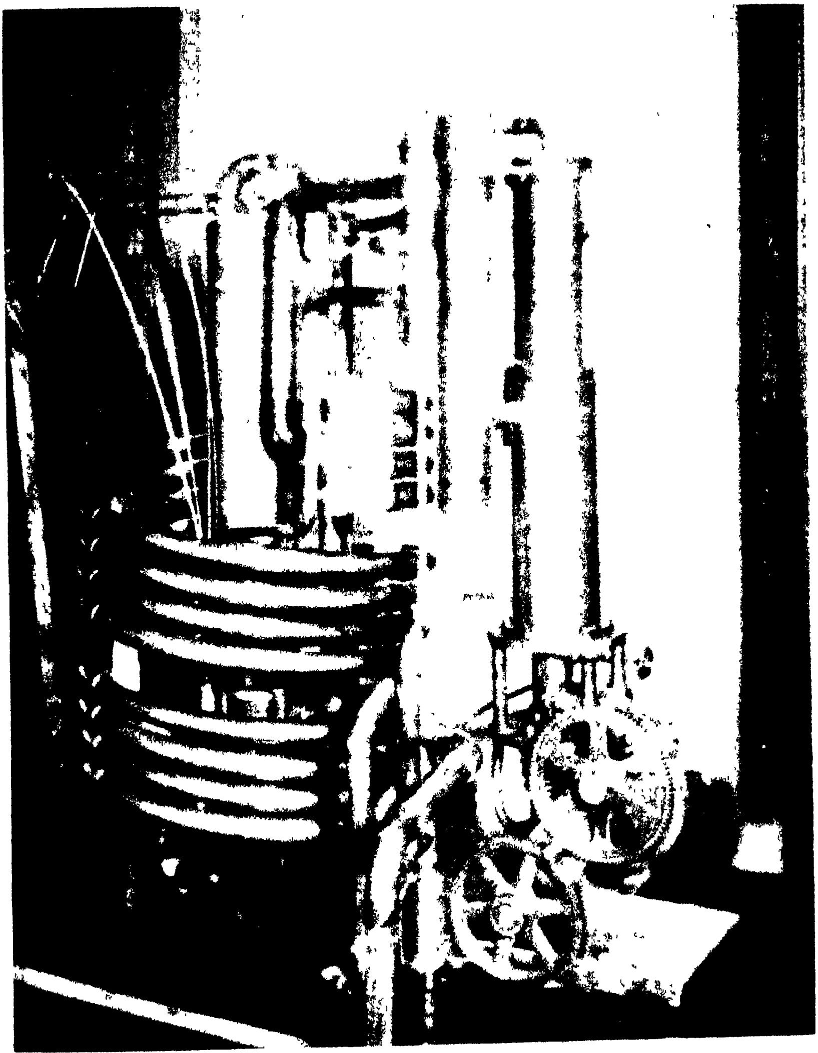

FIG 4 Collins–McMahon airplane unit (M. I T model) with case and insulation removed; interchanger channel switch side

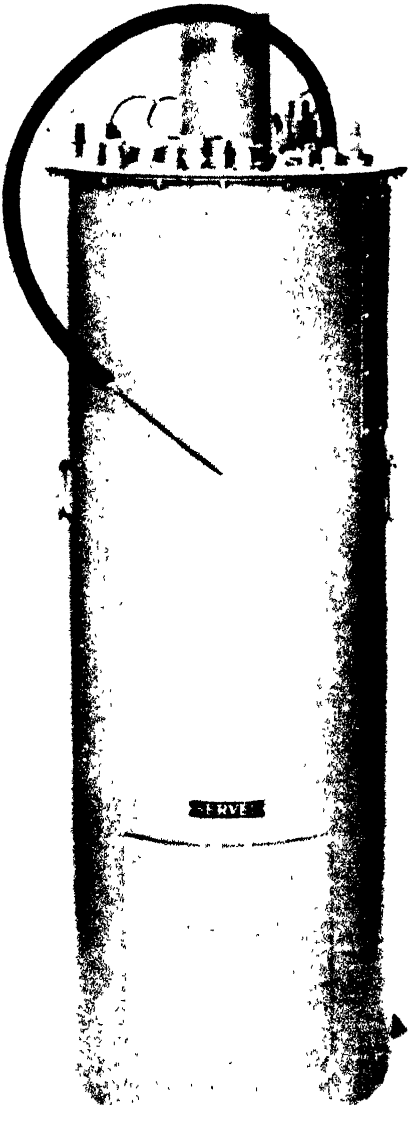

FIG. 5. Submarine liquid-oxygen unit (respiratory oxygen). Capacity 20 lb. per hour of liquid oxygen of 0.995 m.f. purity, 300 lb. per hour air feed unrefrigerated, pressure 3000 p.s.i.g. Capacity 35–40 lb. per hour of liquid oxygen of 0.98–0.985 m.f. purity with feed refrigerated at −40°C.

details of installation of the tubular leads are important, but chief of these is the soldering of one end of a copper wire (16 to 18 gauge) to the liquid tubular lead of cupronickel alloy near its connection to the liquid-oxygen holder, while the other is soldered to a rod of the chassis of the unit to provide a gentle flow of heat to the tube. In this way it is possible to prevent the liquid phase from entering the tube beyond the level corresponding to the bottom of the liquid-oxygen holder.

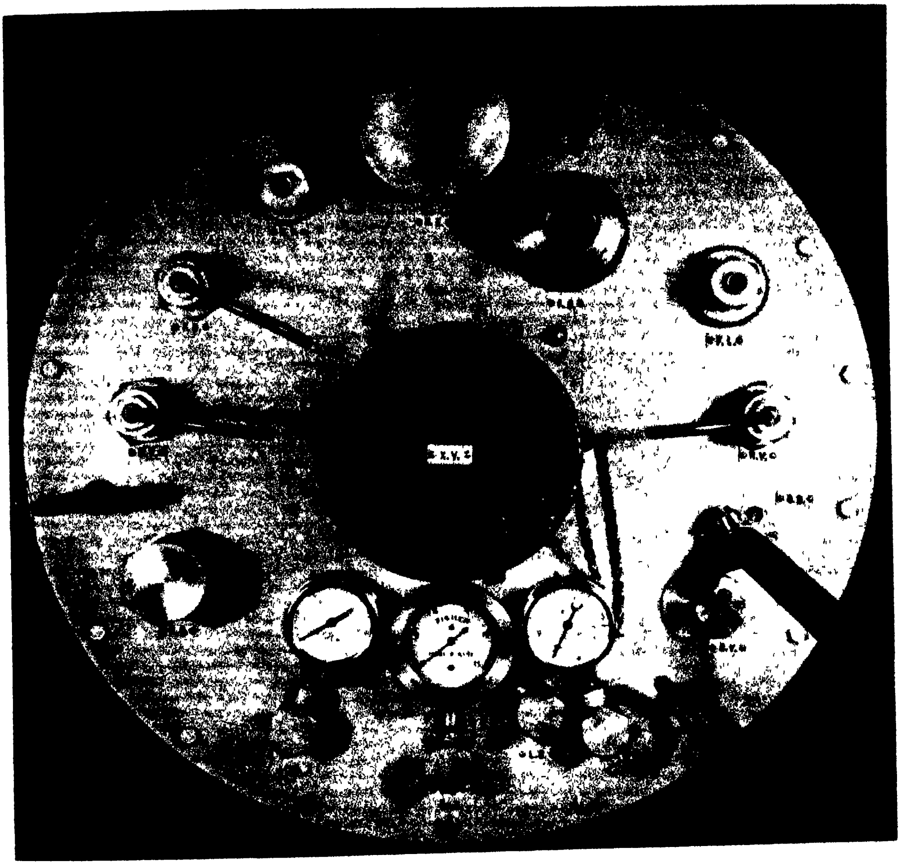

FIG. 6. Top deck of S-unit

H P = high pressure air connection
N E = "nitrogen" effluent outlet
O.D. = oxygen product (liquefied) delivery
L L and L.G = liquid level attachment joints
O V. = hand operated liquefied oxygen delivery valve
R.V. = relief valve on high-pressure line
R.D. = rectifier relief diaphragm
G X = pressure gauge ahead of expansion valve
G.R = pressure gauge to rectifier
X.V = expansion valve cover
F.L. = liquid freon-12 line
F.G = gaseous freon-12 line
F.D = oil drain on freon interchanger
D V = oxygen drain valve

Another important feature of the unit was the means of withdrawing liquid oxygen. The simplest and most desirable plan would be to have the liquid oxygen flow continuously and without attention from the bottom or boiler portion of the rectifier. Use was made of a float enclosed in a cage to which liquid oxygen had access at about the required level above the boiler coils. Access was through holes in the cage covered with monel gauze of 300 mesh to prevent dust particles (solid carbon dioxide) from reaching the valve.

A principal difficulty with a float is the choking of the flow owing to accumulated carbon dioxide dust or other sediment. The seat and needle design was arranged to be self clearing as the float operated, and the seat could be easily removed either for renewal or for inspection through an access cover without dismantling the unit. The delivery of liquid began without attention as soon as the level in the boiler exceeded the predetermined level, and delivery was through a flexible metal vacuum-jacketed hose, visible in figure 5.

The regime of the column proceeds best when the pressure in the column is maintained constant. For this purpose an automatic expansion valve[6] was devised, which obviated the necessity of adjustments once the unit was brought into operation. Ultimately, two principal types of self-adjusting expansion valves were constructed, the second of which can also be used in cases where variations in atmospheric pressure occur (airplanes).

Finally, the unit was provided with a heat interchanger for feed precooling; for by precooling the air feed to −40° to −50°C. the yield of liquid oxygen can be approximately doubled. The Servel Inc. unit (2T-200F), using freon-12, was used with a liquid-freon subcooler.

The clean-up system for the air feed (300 lb. per hour) consisted of two steel tubes containing solid potassium hydroxide used in series, together with a tube of activated alumina. The latter tube contained an electric heater for reactivating the alumina after 50 hr. of use, which was placed in a central tube reëntrant to the alumina container tube. Heat-conducting disks were pressed upon the reëntrant tube before assembly for the purpose of diffusing the heat throughout the alumina without creating too great temperature differences. The entire clean-up system fully charged (70 lb. potassium hydroxide, 70 hr. operation) and with its supporting stand, designed by Servel Inc., weighed about 700 lb. The model unit weighed 180 lb. Units complete with clean-up system were manufactured by Servel Inc. from drawings based on the model unit.

A complete set of operating and maintenance instructions for the submarine units was produced by Mr. Dudley A. Williams with the assistance of Mr. Robert P. Cavileer after many weeks of tests with both the model unit and the units manufactured by Servel Inc.

The purity of the liquid oxygen from the S-unit depends upon the quality of the column or rectifier packing.[7] Originally the requirement was for oxygen of purity 0.95 to 0.96 m.f. The original tests of the model units were conducted at the laboratories of the Air Reduction Company in Stamford, Connecticut, and with the normal supply of 300 lb. per hour of air at 70°F., 17.5 lb. per hour of liquid oxygen in the receiver was obtained of purity 0.975 m.f.[8] The precooling refrigerating unit was not received until the tests at the U. S. Navy testing laboratories at Annapolis were undertaken a month later. With precooling at the −24°F. level, the yield of oxygen of purity 0.95 to 0.96 m.f. was 33 lb. per hour.

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[6] A protective cover conceals the valve in figure 5

[7] The packing in the original S-units was No. 2 Madison shoe eyelets The h.e.t.u. (height of the equivalent transfer unit) was 3.8 in., as shown by tests conducted by Prof B. F. Dodge.

Meanwhile request was received to increase the purity of oxygen in order that the S-unit might be used in applications other than the re-oxygenation of submarine air. It was found possible to raise the purity to 0.995 m.f. by employing the gauze saddle column packing devised by Dr. McMahon, along with improvements in the liquid distributor and an improved anti-entrainment device worked out by Mr. D. A. Williams. Two of the modified Servel units were also forwarded to England, where they were reported to have performed according to the indications given in the D. A. Williams *Instruction Book*.

IV. THE SUPPLY SHIP UNIT

In February 1944 a request was made for an oxygen unit which would produce liquid oxygen or deliver high-pressure gaseous oxygen directly to a manifold to which standard oxygen cylinders could be attached for charging to 2000 p.s.i.g. After the model had been built it was further desired that precooling means be included to increase the yield of liquid oxygen. The purity desired was 0.995 m.f.

A unit of the kind described would have the advantage that no separate oxygen compressor would be required to charge cylinders, a saving in expense, weight, and maintenance of the compressor. Moreover, the oxygen would be delivered absolutely dry and as pure as it was produced directly from the rectifier, i.e., uncontaminated by the operation of compressing in a multistage compressor in contact with warm oil vapor.

The question of the design of the liquid-oxygen pump presented some difficulty, since the unit was to be self contained, which meant that the pump must be driven by the compressed-air feed. There was also the problem of the liquid-oxygen piston leak, for the viscosity of liquid oxygen at 90°K.(0.002 c.g.s. units) is not far from one-fifth that of water at room temperature. Also, the use of piston-rod packing seemed desirable to avoid if possible; and problems of heat leak, gas "lock", valves, and choice of materials entered along with the difficulties posed by lubrication.

For the power or drive portion of the pump there arose the questions of meter-

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[8] The model S-unit was provided with a direct connection or conductor for liquid oxygen from the boiler to the hose. Now the rectifier pressure is about 1 atm. above atmospheric pressure; accordingly, when liquid oxygen is released from this higher pressure there is compensation for the change in state in the form of evaporation of some of the liquid. The loss amounts to about half a pound of liquid per hour. In later units the liquid oxygen was precooled by the effluent, whereby the liquid issued into the receiver slightly lower than the normal boiling temperature.

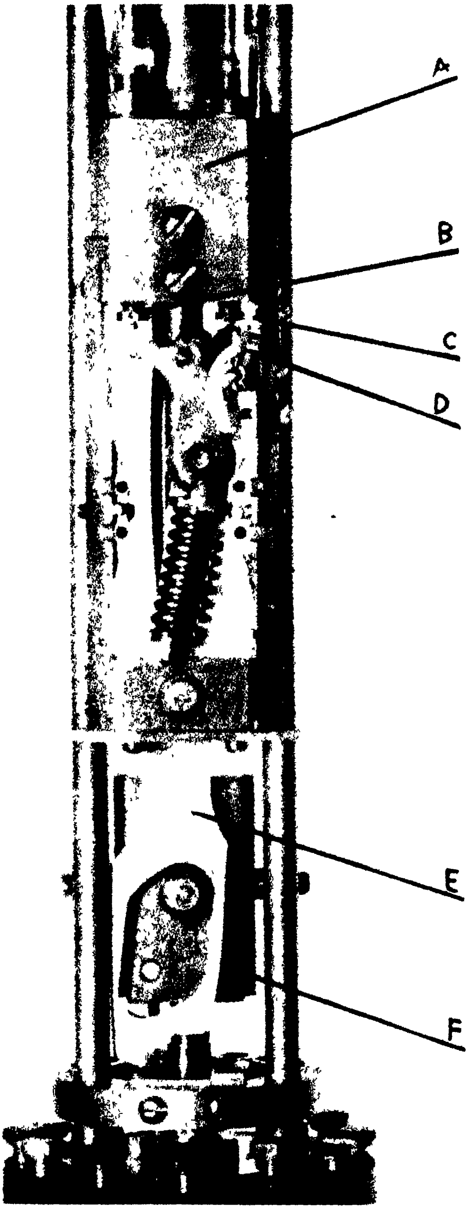

FIG. 7. Liquid-oxygen injection pump. Valve mechanism at beginning of power stroke A, valve block; B, exhaust-valve push rod, C, inlet-valve push rod; D, latch to hold inlet valve open until loaded spring mechanism is just past the equilibrium position in the direction of opening the exhaust valve, E, cam arm at beginning of power stroke; F, roller block rigidly fastened to piston rods

ing the air charge, the durability of materials, heat insulation, lubrication, and speed control,—to refer to the principal items. As far as is known, no air drive for compressing a cold liquefied gas has been described.

One obvious recourse in the case of the oxygen piston would be to use a hardened nitralloy piston and cylinder for the liquid-oxygen compression, employing as close a fit as permissible. A piston-rod packing would be required if this expedient were adopted, but the packing need not have to resist the full pressure of the desired oxygen pressure (2000 p.s.i.). The amount of leak for such a piston cylinder is easily computed, using Poiseville's Law for an annular clearance. Thus the weight, W, of liquid oxygen escaping under a pressure difference Δp is given with sufficient exactness by the expression

$$W = g\,\frac{\Delta p}{L} \times \frac{\pi D \bar{\rho} t^3}{12\mu}$$

where D is the piston diameter, L the length of the leak path, $\bar{\rho}$ the mean density, and t the annular clearance (difference between the radii of the cylinder and the piston). For a clearance of 0.0002 in. the leak is 4.53×10^{-3} lb. (2.06 g.) per second of exposure to a pressure difference of 2000 p.s.i., assuming D = 0.75 in., L = $\frac{1}{4}$ in., and $\mu = 1.34 \times 10^{-4}$ lb./ft. sec. If the travel or stroke of the piston could be accomplished in 1/20 sec., the leak would be but 0.1 g. or about 1.2 per cent of the leak of the full charge for a 1-in. stroke. The attempt was made, however, to devise a piston self sealing against leak, which would also obviate the possibility of metal-metal contact.

The pump completed for the model unit was contained in a case in two sections separated by a 2-in. thick heat barrier. The case was 3 in. in diameter, the upper section was 20$\frac{3}{8}$ in., the lower section 14 in. in length. Both the power piston (in the upper case) and the oxygen piston were designed to be self sealing through the use of piston rings made of cordovan leather. The leather, however, was compressed to about 5000 p.s.i. prior to cutting and finishing the rings, and the annular area normal to the piston axis was adjusted to approximately double the unit pressure imposed upon the piston. The amount of the expansion of the leather rings in the case of the power piston was limited by the brass-piston design to about 0.002 in. on the diameter. The leather was soaked in a high-pressure lubricant mixed with very finely powdered natural graphite prior to mounting the assembly of leather and brass spacing rings. The cylinder liner was of high polished nitralloy. No appreciable leak of air past the piston was observable with 2000 p.s.i. air pressure after considerable operation.

The oxygen piston was constructed similarly to the power piston, but of course had to be used without liquid lubricant. The metal employed was beryllium-copper. The cylinder, 0.75 in. in bore diameter, was of the same material, but after heat treating to obtain maximum hardness the inner surface was lapped and highly polished. The diameter of the metal base of the oxygen piston was made 0.004 in. smaller than the cylinder base and slightly tapered toward the ends. At one end flexible connection was made with the piston by means

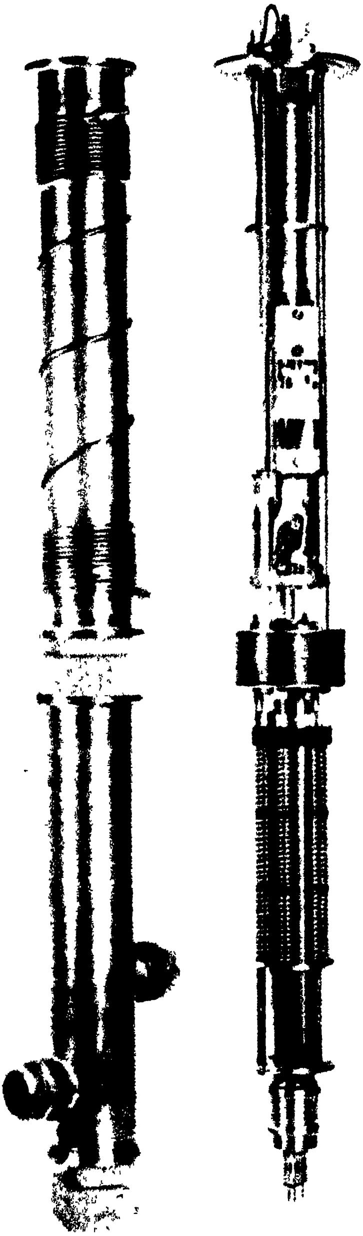

FIG. 8. Pump No. 2 and pump cases

of a split threaded locking piece, as a means of obviating any slight misalignment of rod and piston.

The rings were assembled as follows: First a single leather ring (0.040 to 0.050 in. thick), next a 0.09375-in. thick fine-texture graphite ring followed by two leather rings, a beryllium-copper ring (0.004 in. less than the cylinder in diameter), two leather rings, a brass ring, and a single leather ring. The middle ring was again graphite, and the arrangement was repeated in inverse order to that above described. There was therefore a total of twelve leather, four beryllium-copper, and three graphite rings.

The cutting of the leather rings and their adjustment to final size proved to be an exacting problem. Also, before use the fat or oil with which the leather is impregnated must be extracted (with xylol); upon doing so it will be found that the leather is entirely flexible at liquid-hydrogen temperatures.[9]

It will be perceived that the contraction of the various substances must be known and allowed for; otherwise, too great friction or too loose a fit will result. The function of the graphite rings is particularly important. They were used principally as a means of preventing contact of the metal portions of the piston with the cylinder wall under sudden thrust, because at low temperatures metal surfaces on contact appear to abrade much more readily than at room temperature. The quantitative aspect of the temperature contraction is as follows: The mean coefficient of contraction from 20° to -190°C. observed for the graphite used was 3.5×10^{-6} cm. per 1°C. per centimeter length. The same coefficient for the beryllium-copper proved to be 12.5×10^{-6} in the same units, while the leather (dry) gave a coefficient of 32×10^{-6}. The metal cylindrical base upon which the rings were fitted was 0.5 in.; the outside diameter of the rings was 0.75 in.

There will be an axial contraction on cooling as well as a contraction along the diameter. The importance of the axial contraction lies in the fact that it is necessary to limit the amount of the dilation of the compressible leather rings to avoid excessive friction. The setting of the stop, which is obtained partly by the use of leather rings of slightly varying thickness and finally by machining a metal part of the piston, is of course done at room temperature, and a value is determined which will result in an effective cylinder wall seal at liquid-oxygen temperatures.[10]

Because the graphite has a smaller contraction it is possible to adjust the diameter of the ring at room temperature to a value which will leave it with a fit to the cylinder of 0.0001 in. at the operating temperature The leather is not perfectly uniform in thickness, and when the sudden thrust takes place at the power stroke the presence of the graphite rings insures that no metal metal contact occurs and the piston alignment is accordingly preserved. The graphite is also anti-frictional and no wear has been observed against polished beryllium-copper.

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[9] Space is not available here for all the details of the various operations. However, the more important steps in the solution of the several problems are presented The author will be glad to supply details, through private correspondence, to those interested

[10] Some concern regarding explosive hazard is justified in the absence of positive knowledge when leather is brought into contact with liquid oxygen. The author had not been able to ignite pieces of leather on transferring them rapidly from a jar of liquid oxygen to an adjacent flame. The amount of leather in actual contact with liquid oxygen in the case of the piston is very small (0.05 cc.)

The adjustment of the movement of the metal piston parts controls the degree of expansion of the leather rings and may be considered in the light of the temperature contraction data given. The axial contraction for an actual piston is given in table 1.

This amount of contraction enlarges the gap or distance through which on application of pressure the leather will be compressed, or the leather would be compressed too much. Now the diameter contraction is 0.0030 in. and allowance can be approximated for the axial contraction by computing the relation between the change of thickness of the leather and the unrestricted increase in diameter resulting from compression normal to the plane of the ring. The formula is found to be, on the basis of no net volume change:

$$\delta D = \frac{\delta l}{t_0} \times \frac{D_0}{2}\left(1 - \left(\frac{D_1}{D_0}\right)^2\right)$$

TABLE 1

Temperature contraction for a temperature drop of 210°C.

Leather	0.528 in. × 210 C. × (32.0 − 12.5) × 10^{-6} = 0.00216 in.
Beryllium-copper	0.240 in. × 210°C. × (12.5 − 12.5) × 10^{-6} = 0.00000 in.
Graphite	0.281 in. × 210°C. × (3.5 − 12.5) × 10^{-6} = −0.00053 in.
Net contraction	

Taking the total thickness of the leather rings given in table 1, t_0 = 0.528 in., and the value of δl to be compensated as 0.00163 in., it is found that a diameter increase of 0.000643 in. would ensue under no lateral force if the leather were reduced in thickness by pressure by 0.00163 in. Therefore the gap must be adjusted not to allow 0.003 in. lateral expansion at room temperature but 0.0030 − 0.000643 in. or 0.00236 in. In practice the pistons were run in at room temperature for several hours before adjustment to a gap giving a diameter increase of 0.0025 in. under full compression at room temperature.

The air-driven oxygen piston pump operated very well in the model unit after experience had guided the development. However, the model pump unit (figure 10) could not be operated continuously for long periods, owing to lack of facilities and personnel. Indeed, testing of all kinds was carried out by Mr. D. A. Williams, Mr. R. P. Cavileer, and Mr. T. E. White using air compressors whose upkeep consumed a large portion of their time and energies. As a consequence a second pump was constructed and sent to the Independent Engineering Company at O'Fallon, Illinois, for continuous accelerated test at room temperature. Through these tests many deficiencies of design detail and of durability were revealed and corrected. The more important of these items were the wearing qualities of the bearings of the valve-actuating mechanism, air-valve durability, valve push-rod packing characteristics, valve-spring life, permanency of adjustments, properties of the self-sealing air piston, the durability of the 2-in. thick bakelite gear-stock heat barrier separating the oxygen portion from the power portion of the pump, the durability of the brass springs used to accomplish the return stroke, the wear qualities of the dry leather piston-rod packing in the heat barrier, to cite principal items.

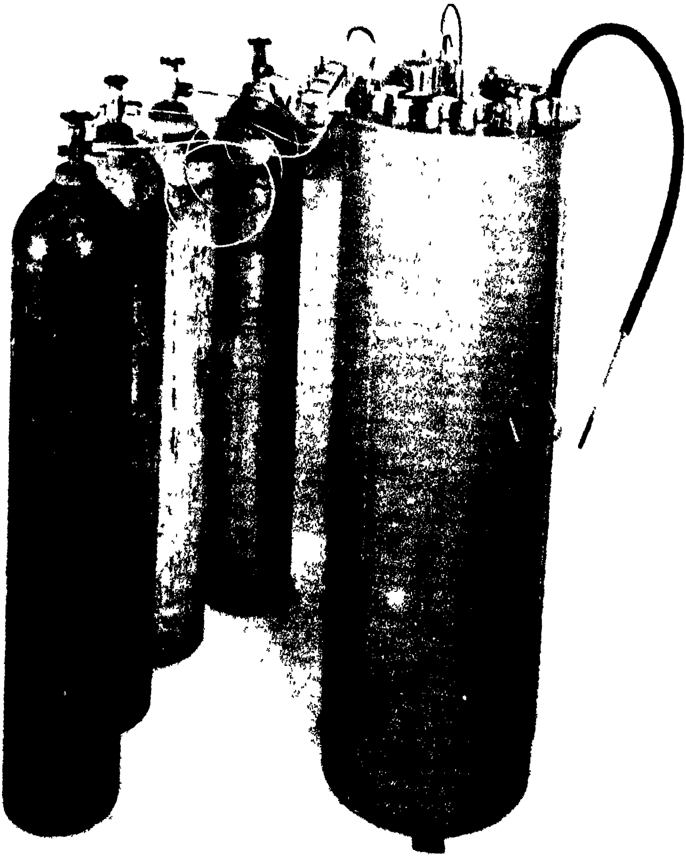

FIG. 9. Pump unit with rotating column for producing either liquefied oxygen or high pressure gaseous oxygen

During the first stage 537,600 strokes (nominally equivalent to 450 standard tanks filled) were completed before a breakdown due to failure to lock securely the compression-limiting locking nut on the oxygen piston. The second stage saw 467,700 strokes completed. The cause of failure was fatigue of a hardened

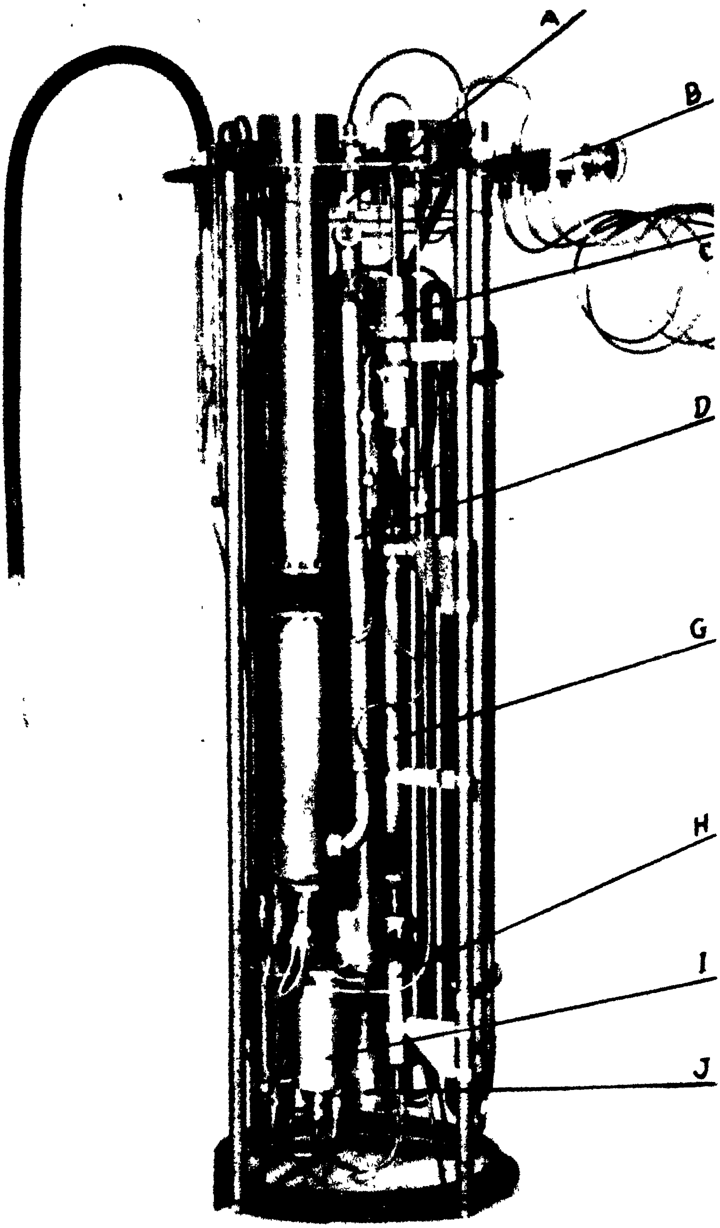

FIG. 10. View of pump unit No. 3. A, air admission valve to power section of pump; B, high-pressure oxygen-gas delivery manifold, C, automatic expansion valve; D, effluent delivery from rectifier; G, filter; H, charcoal adsorber for hydrocarbons following boiler coil, I, float case; J, rectifier boiler.

part of the valve-actuating mechanism but the valves, having run for over a million strokes, were badly worn and a change in design was begun which probably has not yet been sufficiently extended. No appreciable bearing wear was observable, although intentionally no lubrication had been employed on the valve-operating gear. The third period comprised 330,000 strokes. During this test, however, several innovations were under examination, particularly directed toward developing valves of long life. The fourth period ran to 466,356 strokes, when the brass return-stroke springs collapsed completely at a total of 1,801,656 strokes. The entire return spring system was changed as a result of the test.

Moving pictures of the operating pump taken by the Independent Engineering Company's personnel indicated that the free-running pump at room temperature completed its power stroke in less than 0.02 sec., roughly the limit of the speed of the camera. The maximum speed of the three pumps which have been constructed is 240 strokes per minute. However under load, pumping liquid oxygen at 2000 p.s.i., the power stroke requires a much longer time, depending only partly upon friction of the oxygen piston, as was indicated by using a nitralloy piston where no appreciable piston friction could develop, and partly on the added time required to load the power piston with the compressed air. In its present stage of development the working speed has not been brought to exceed fifty to sixty strokes per minute, equivalent to the same number of pounds of oxygen per hour. There developed however an unexpected difficulty, the description of which may be of interest.

The model pump unit (figures 7 and 8) was completed and installed in the winter of 1944 when atmospheric moisture was negligible. The model pump unit on test at the Independent Engineering Company performed satisfactorily on test periods extending to over 60 hr. when the tanks were filled to pressures exceeding 2000 p.s.i.[11] The course of the tests was finally terminated, owing to the fact that acetylene gained access to the compressor air intake and, finding its way to the oxygen cylinder of the pump, exploded and demolished the pump.

The second example of the pump was forwarded for installation in one of the larger pump units described below but was held in the humid midwest summer climate some time before installation. The leather rings of the oxygen piston absorbed enough moisture during the delay to bring about a volume change in them sufficient to cause great friction on the pumping stroke and consequent malperformance.

It was later found that the defatted leather does change volume greatly on exposure to moist air. Of course, special packing cases could be devised which would prevent access of moisture to the leather, but time and opportunity to do this were lacking. It is not altogether unlikely that certain substances might be adsorbed on the defatted leather which would destroy the extraordinary affinity

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[11] A request was made to pump oxygen to pressures of 3500 p.s.i.; this the pump accomplished without any detectable leak at the oxygen piston.

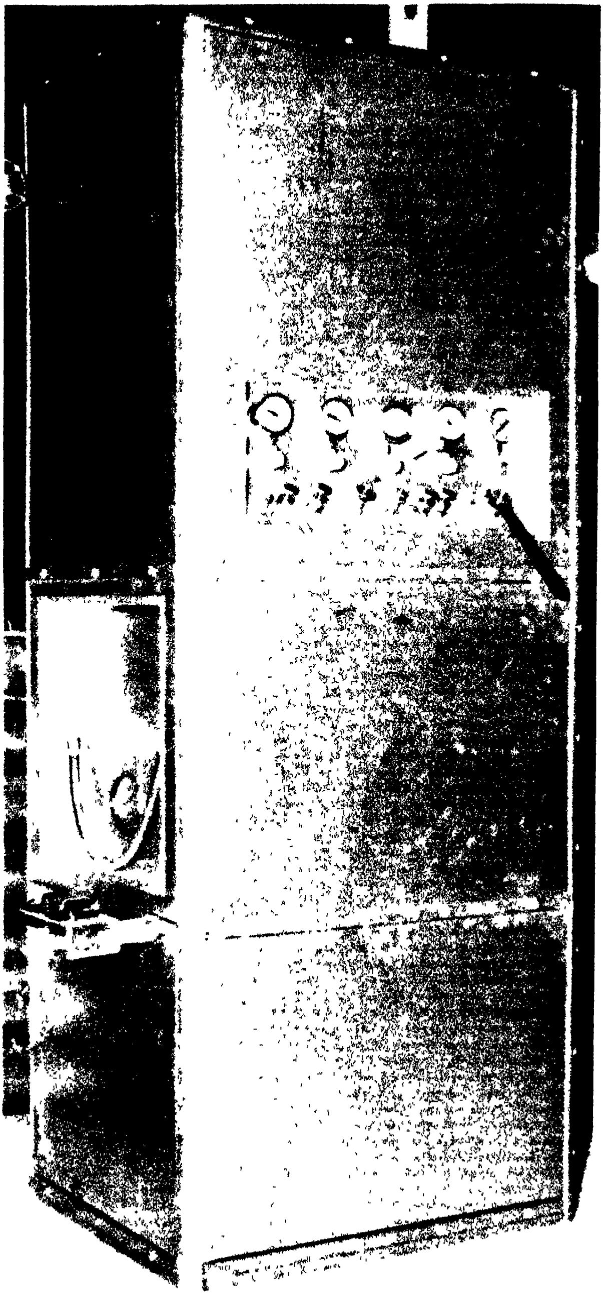

FIG. 11. K30MS unit. Precooled-feed dual-purpose unit to produce 70 lb. per hour of liquid oxygen or high-pressure (2000 p.s.i.) oxygen gas.

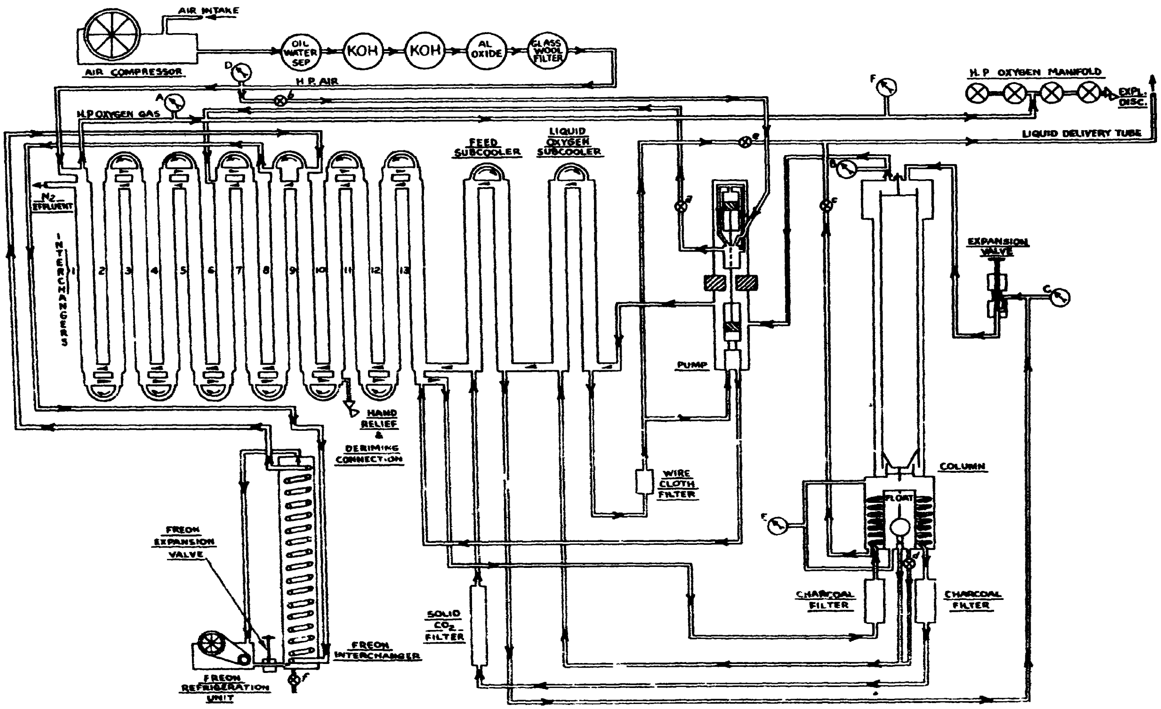

FIG. 12 Flow diagram of large pump unit for use with high-pressure air feed.

A = high-pressure oxygen 0–3000 lb pressure gauge
B = rectifier 0–50 lb pressure gauge
C = high-pressure expansion valve 0–4000 pressure gauge
D = air inlet 0–4000 lb pressure gauge
E = liquid-level gauge 0–15 in of water
F = oxygen manifold 0–3000 lb pressure gauge
a = air-exhaust pump valve

b = air-inlet pump valve
c = boiler drain valve
d = gas valve
e = liquid valve
f = oil drain
g, h, i = air switchover valves for freon interchanger

of the defatted material for water, but experiments in this direction are uncompleted.[12]

V. THE LARGE PUMP UNITS FOR USE WITH HIGH-PRESSURE AIR FEED

The decision was taken by the division of the N.D.R.C. in control of oxygen development to construct two units along the lines of the model pump unit but with the addition of precooling means to satisfy the interest in larger quantities of liquid oxygen. The units were also to be twice the capacity of the model unit and to have rotating columns. The units were to be constructed by the Independent Engineering Company but the design was the problem of the M. I. T. group.

The experience available for the design of the two units was limited to the small model unit and such intimations regarding deficiencies or inadequacies of design as had come to light through tests of the model unit, which through lack of facilities could not be pushed as far as was desired. The general features of the design were as follows:

Instead of the cylindrical shape with instruments and connections on the top surface used for the S-unit (figure 6), dictated by the small space available for installation, another design was envisaged. The unit proper was built into or the parts mounted in a strong rectangular-section steel chassis consisting of rigid steel plates at top and bottom connected by heavy-walled steel tubing. Outside of the chassis a covering of the Lindsay type was adopted. The resulting aspect of the unit was a rectangular shape some 80 in. in height and 22 x 32 in. in section with connections and instrument panel, vacuum-jacketed delivery tube panel, and drains all recessed to present plane surfaces (figure 11). The flow diagram is given in figure 12.

The elements of the unit will be described in their principal features, beginning with the air feed. It scarcely needs comment that the units represent a stage in the development of the type rather than a culmination. Extensive tests on the units were not completed at the time the contract terminated, but sufficient information was obtained to indicate some of the design modifications and improvements which would be desirable.

A. *The Joule–Thomson–Siemens interchanger*[13]

The model unit was equipped with an interchanger of the encased seven-tube variety, which in some respects is very well adapted to serve the purpose of the type interchanger. In the first place the mass distribution may be dealt with advantageously, since the central tube may be used for the feed, one of the six surrounding tubes for gaseous oxygen, and the remaining five tubes for the nitrogen. Relative to a weight unit of air there is 1/4.3 of pure oxygen and 1/1.3 of "nitrogen", so that the heat-transfer surface available to each fluid bears a rough approximation to the weight fractions nature has established for the principal components of air. In the second place the situation may be dealt with more easily than some other types in applying the algebra of design for computing the heat transfer and dimensions of the constituent metal parts. In the third place the interchanger is easily assembled and bonded as by soldering.

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[12] The present design of pump could be easily adapted for motor drive, but a speed control would have to be devised which would duplicate the nicety of control attained by regulating the time of exhaust in the case of the air drive The motor drive would also make variations in the friction characteristics of the expansible leather rings of the piston of little or no practical importance. A disability of the ordinary motor drive, however, is the difficulty of devising a rapid power stroke (1/10 sec. or less) with controllable slow return stroke, a feature of the air drive which is very attractive.

[13] The author is aware that "Joule–Thomson interchanger" is the designation usually employed for this heat interchanger. The record shows, however, that neither Joule nor Thomson had anything to do with this type of interchanger, whereas William Siemens filed a patent on the device in 1857, or at least a device whose principles are embodied in the heat interchanger used by Hanson and Linde in the 1890's for the production of liquid air. In what follows the interchanger will be referred to as the J–T–S interchanger

The interchanger was to be used for high-pressure oxygen production and if desired also for liquid-oxygen production. Since the simple type still or rectifier was to be employed, at most some 0.65 weight fraction (w.f.) of the total oxygen was to be extracted from the feed (0.75 w.f. approximately is the limit), or 15.1 lb. of oxygen per 100 lb. of air feed. When gaseous oxygen (2000 p.s.i pressure) was being produced the interchanger would operate in mass balance and heat-capacity unbalance. In the production of liquid oxygen both mass and heat-capacity unbalance results.

The high-pressure oxygen channel of nickel-copper alloy (0.70 copper and 0.30 nickel, 0.155 in. O.D., 0.015 in. wall) was placed coaxially in the central feed tube of nickel-copper alloy; the six surrounding tubes (0.523 in. O D., 0.025 in. wall) and the twelve channels comprising the spaces exterior to the outside diameter of the seven tubes and the case were available for the effluent.[11] It was desired that the pressure drop for the effluent channel should not exceed 5 p.s.i.g., and considerations of design indicated that a tube having an outside diameter of 1.625 in. should be used for the case. Standard fittings are available for ends, and the oxygen channels were connected from one section to the following by means of special castings into which the channels and interconnecting tubes were silver soldered. The total length of each of the thirteen sections was 54 in., making a total of 58.5 ft.

The effluent before reaching the J-T-S interchanger passed from the top of the rectifier through the case surrounding the oxygen end of the pump, thence through a liquid subcooler, and a subcooler for the air feed on its way to the expansion valve. The first of the foregoing three cooling stages was to maintain the pump oxygen cylinder below the temperature of the incoming oxygen as a measure preventing vapor lock;[15] the second to enter the liquid oxygen to the pump well below the boiler temperature to create loading pressure and also when producing liquid oxygen to eliminate "flash gas" loss on delivery to the containers. The liquid-feed precooler, by diminishing "flash gas" when the liquid air leaves the expansion valve, diminished certain difficulties of head design.

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[11] The design of a three-channel interchanger presents some features which appear not to have been dealt with, as far as can be determined from a far from exhaustive search of the literature.

[15] Calculation shows that liquid oxygen on adiabatic compression to 2000 p.s.i. heats about 3°C.; thus cooling of the oxygen injection cylinder also removes this heat

The feed channel is interrupted at a point of its course for the connection of the freon-12 interchanger for precooling the gaseous air feed. The freon refrigerating units are designed to allow the freon vapor to leave the refrigerator coils at nearly the temperature of the coil. Also at the temperatures employed, −45° to −50°C., a liquid-freon precooler was employed cooled by the cold return vapor. For 540 lb. per hour feed an 8-horsepower (0.8 ton) refrigerating unit was employed, a size which proved satisfactory in service.

Under conditions out of complete control it may happen that water will be incompletely removed from the feed, in which case it is convenient to be able to interrupt operation for the purpose of warming the J–T–S interchanger to remove the water. For this purpose a relief-valve connection is incorporated at a point in the feed channel beyond which ice will not collect. By means of a warm air current the light-weight heat interchanger is quickly warmed, the ice plug melted, and the water blown out. By this device a prolonged shut-down is avoided and normal operation quickly restored.

It will be noted on the flow sheet (figure 12) that high-pressure air near the entrance to the unit is taken by a branch line connecting to a coil soldered to the upper or power side case of the pump. The coil is connected on its cool side to the feed at a point further down stream. The purpose served is to remove refrigeration reaching the upper pump case and prevent the valve mechanism from cooling. It will be observed that the refrigeration lost by cold leak is partly recovered.

B. The rotating column

The column is considered to include the head and boiler with its feed coil, float, and other parts relating to the operation of distillation.

The bearings of the rotating part (10 to 12 R.P.M.) which contained the column packing were made of beryllium-copper for the races and stainless-steel balls. The thrust bearing was mounted on the top of a pedestal supported on the float cage and braced by a cast-alloy spider supported from the walls. The upper bearing and shaft were contained in the head, and when the cover was removed the column could be easily lifted out of the column case. The use of a skirt at the lower end of the column permitted the use of a liquid-oxygen seal for the bottom of the column.

The column head is a matter of considerable importance, for the design must allow the liquid to be evenly distributed over the packing and at the same time liquid feed must not be entrained by the current of vapor passing up the column. The difficulties of the situation will be perceived to be enhanced by a species of discontinuity peculiar to the type of rectifier used. Thus liquid air passes to the rectifier from an expansion valve where liquid is accompanied by 10 or more per cent of its weight of gas at substantially the rectifier pressure. The liquid and gas mixture is discharged into the rectifier head, the gas creating with the upcoming vapor a junction involving a sudden velocity increase. This is the discontinuity referred to and it can be the seat of considerable entrainment of liquid feed if the velocity of the vapor in the column is near the critical velocity and the discontinuity occurs in the packing.

To avoid the vapor velocity discontinuity in the packing Mr. D. A. Williams designed a head comprising the following features: The liquid air and flash gas were received from the expansion valve into a space from which the mixture passed to an annular box soldered to the top of the rectifier cover. From the under side of the box twelve tubes projected the mixture tangentially into a bowl which was mounted on the top of the rotating column. In the bowl the vapor separated and passed out at the top to join the vapor leaving the packing from its last contact with the liquid which by gravity flow was discharged through multiple tubes over the top of the packing. By this means a vapor velocity discontinuity *in the packing* was avoided, and no entrainment takes place unless the vapor velocity through the packing exceeds a value characteristic of the particular packing used.

There is, however, another discontinuity at the bottom of the column which caused considerable difficulty during tests of column packing in the model pump unit. The bottom support for the packing was originally designed to be a cone formed of perforated brass. The angle of the cone was finally chosen of a value which would present a total area of perforation openings equal to the cross-sectional area of the column.[16] This provision, however, did not allow the liquid to drain regularly from the bottom of the column. After attempting various devices Mr. Williams, acting on a suggestion of Dr. Teeter, placed a number (twenty-four in one test) of $\frac{1}{10}$-in. thin-walled drain tubes suspended from the packing support plate. The device proved to be very satisfactory. The liquid hold-up or instability effect is most evident when the column regime is changed abruptly, as by increasing the throughput rapidly, and was exhibited by various eyelet-type packings and also the metal-cloth saddles devised by Dr. McMahon. The latter, however, exhibit superior throughput characteristics without flooding relative to the eyelets, except possibly the Madison No. 2 eyelets.

C. The boiler coil

The design of boiler coils was based on the heat-transfer data for liquid oxygen supplied by Professor W. F. Giauque (1). The temperature difference between the incoming gaseous feed and the liquid oxygen amounts to about 65°C., which makes for very poor heat transfer in the first section of the coil. The final design and mode of fabrication were worked out by Mr. Williams. Figure 13 exhibits the winding frame and the finished coil. The spacing is very important because of the Leidenfrost phenomenon and extremely violent boiling along the first section.[17] The incoming warm feed enters the outer turns of the coil. It is also proved good practice to provide for a low vapor velocity in the space immediately above the coil.

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[16] If θ is the half-angle of the cone ($\theta < \pi/4$), and n the number of screen openings per unit area each of area a, then $\tau\theta = na$. For a perforated plate of total hole area ratio 0.5, θ is about 27°.

[17] Observations were made of the boiling induced in a typical boiler coil set up in an unsilvered Dewar tube. The turbulence in the liquid surpassed expectations and made evident qualitatively the need of working out the coil design to allow the gas bubbles to escape freely from between the multiple turns of the coil.

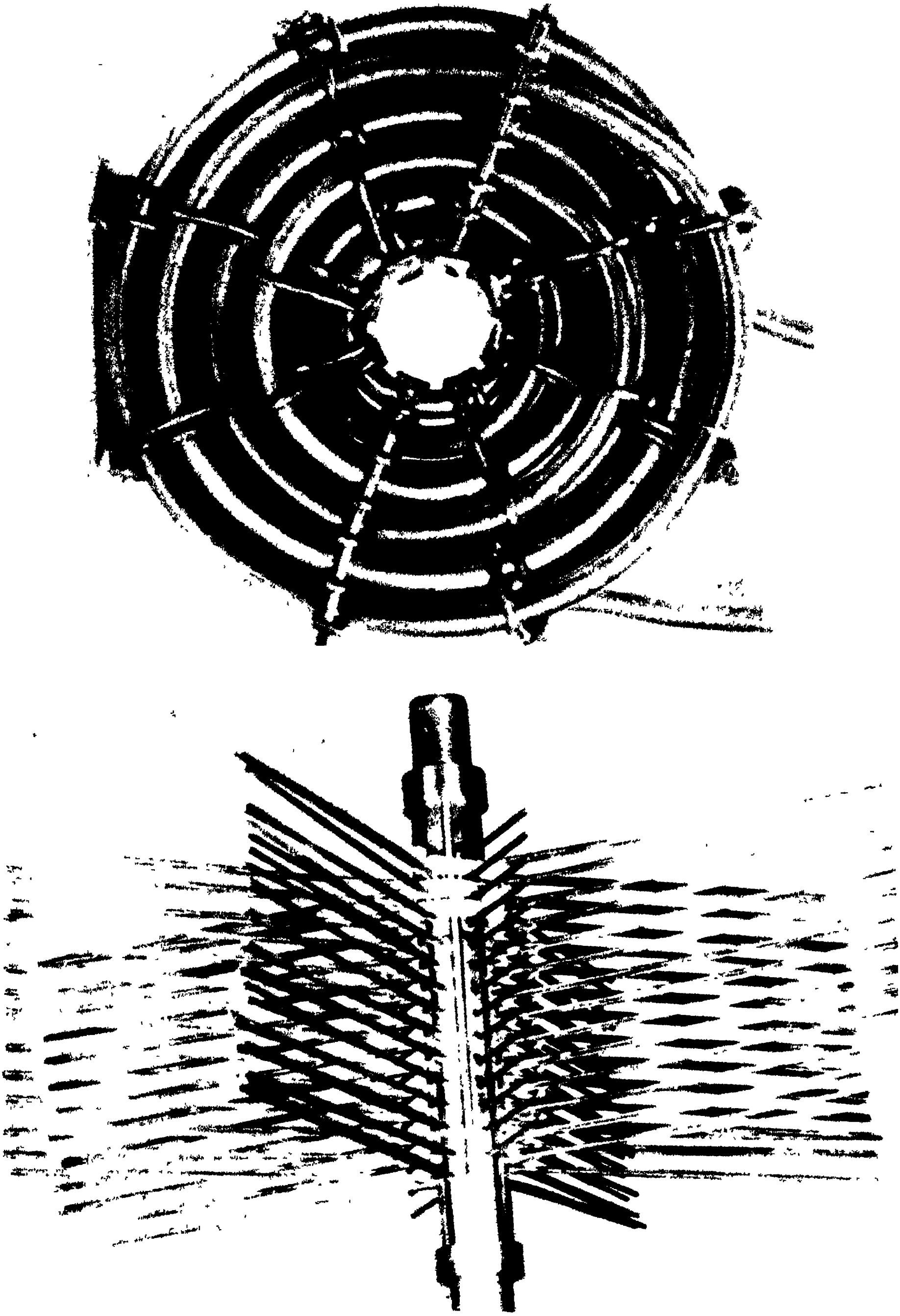

Fig. 13A

The flow diagram (figure 12) shows the presence of charcoal-filled tubes through which the feed passes in the dense gaseous state into the boiler coil. This provision was for the purpose of intercepting by adsorption any acetylene or traces of hydrocarbon vapors. The amount of steam-activated charcoal used in each tube was about 100 g., and it is important that the adsorbed water be driven from the charcoal by heating to 150°C. prior to installation; otherwise the activity and retentivity of the charcoal for the hydrocarbons are markedly reduced. An additional object was to catch any solid carbon dioxide which experience seemed to indicate deposits on the interior of the boiler coil with attendant reduction in heat transmission. The major purpose, however, was the interception of hydrocarbons.

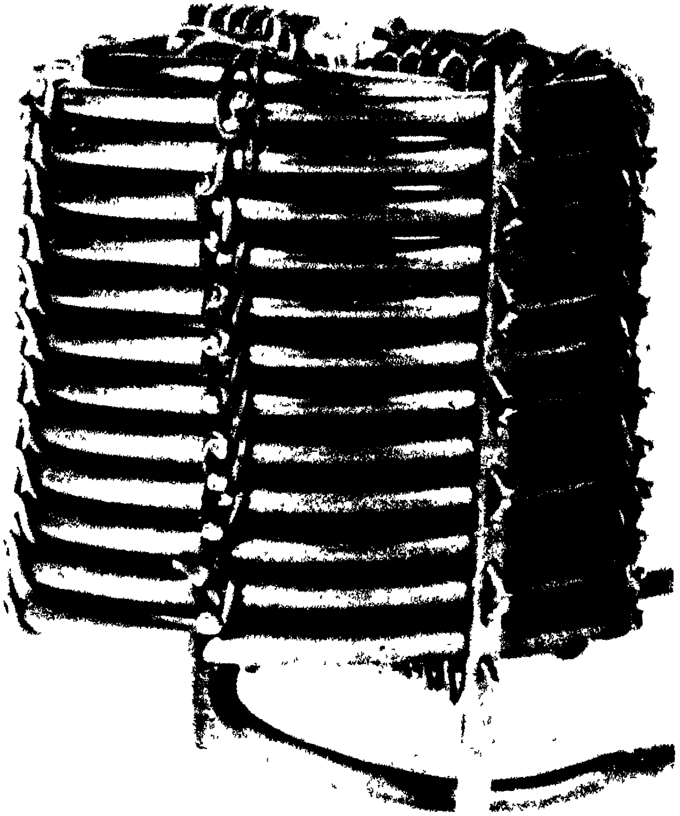

FIG. 13B

FIG. 13A and B Boiler coil spacer and finished coil (devised by D. A. Williams)

The second charcoal and filter tube through which the compressed liquefied air passed was intended to catch any particles of solid hydrocarbons or hydrocarbons in solution in the liquid air[18] and on the felt filter, a final guard against particles to insure freedom from clogging at the expansion valve. No trace of sediment was ever observed in the liquid oxygen delivered by the test units except when quantities of gasoline vapors or acetylene detectable by odor from nearby trucks and an acetylene generator gained access to the compressor intake for a considerable period of time.

D. Column packing

The question of the design and control of packing for columns turns on many factors, and the quantitative state of knowledge is insufficient for consolidation of known factors into a satisfying and coherent theoretical structure. However, the convenience of the packed columns where lightness and rapid attainment of a steady regime is desired needs little urging. In the case of the S-units, recourse was had to Madison No. 2 brass shoe eyelets,[19] a 3.8-in. height of which was equivalent to a plate of the conventional[20] column as obtained from distillation tests on liquid air. The weight per liter is 1.77 lb.

Another eyelet type, No. 3 short eyelets, exhibits a considerably shorter height equivalent—namely, 3.3 in.—based on the use of the test mixture benzene–carbon tetrachloride. The throughput characteristics are, however, somewhat inferior to those of the Madison No. 2 eyelets and also the weight per liter is 2.2 lb.

The metal-cloth ¼-in. saddles devised by Dr. McMahon gave on test with the benzene–carbon tetrachloride mixture a 2.8-in. height equivalent, and the weight per liter is most favorable, 0.94 lb.[21] Many actual column tests with the pump unit in the course of air distillation seemed to indicate little choice between the No. 3 short eyelets and the McMahon saddles, but the throughput characteristics were definitely superior in the case of the saddles. For the shipboard units, special No. 3 short eyelets were made of 0.006-in. thick metal of weight about 1 lb per liter. The unit with case and packing removed is represented in figure 14.

In the distillation of liquid air it is necessary to consider the fact that where oxygen of 0.995 m.f. or higher purity is desired, the impurity is substantially all argon; consequently the bulk of the argon must escape with the nitrogen or accumulate in the column to the detriment of the oxygen purity. It will be observed that where 0.96 to 0.98 m.f. purity is desired, the amount of argon retained by the oxygen will be large and the problem of argon disposal through the effluent is not a problem.[22]

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[18] Certain oils have been observed to dissolve in liquid oxygen in small amounts.

[19] Obtainable from the United Shoe Machinery Company of Boston, Massachusetts.

[20] More correctly, the figure is a measure of the height of a transfer unit.

[21] Thanks are due Professor Avery A. Morton for the distillation tests which led to the numbers given.

[22] No data have been found bearing on the solubility of solid argon in liquid oxygen, liquid nitrogen, or mixtures at temperatures below the freezing point of argon. At a rectifier pressure of 1 atm. the effluent temperature would be 78.2°K., which is lower by 5.71°

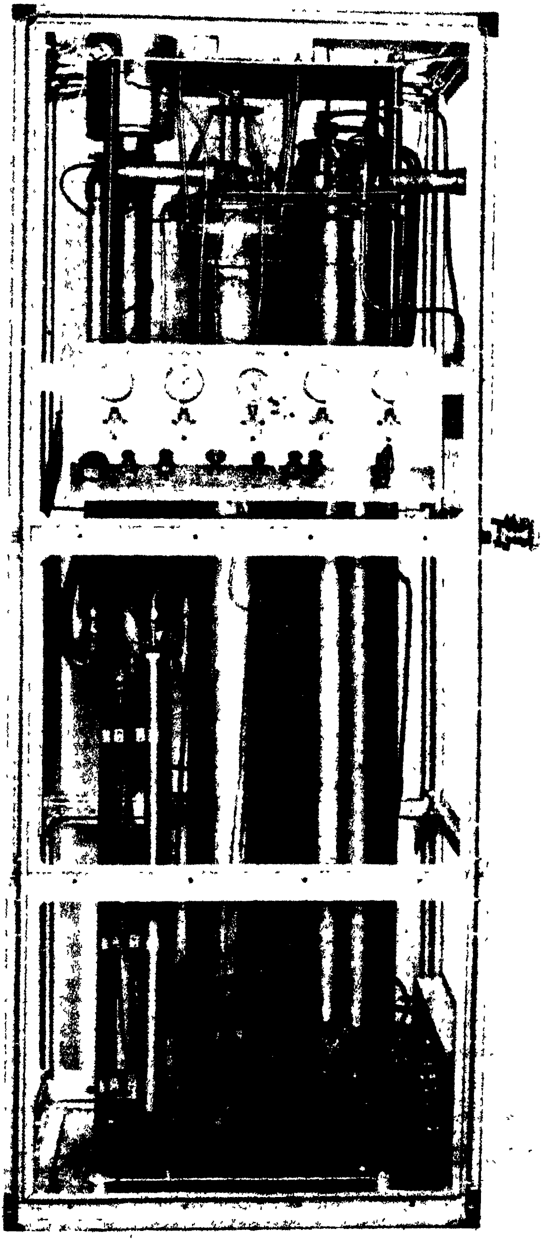

FIG. 14. K30MS unit. Oxygen gas manifold at the right; flexible metal delivery hose at left (not shown); in the center of the chassis is the rectifier with the pump at the left and interchanger on the right; the lower right side of the chassis contains the panel for all drains and purge lines.

VI. PROBLEMS SUGGESTED

The brief sketch given above of the major tangible results of the effort of the M. I. T. group to assist in the development of small, short-period operation oxygen producers does not make explicit mention of various problems which the striving for practical results brought to light and emphasized as important for future research. In what follows reference will be made to a few of these instances in the hope that the younger students of science or engineering may find the subjects interesting and on this account worthy of being taken up with a view to providing invaluable new information.

The most recurrent difficulty was perhaps the almost entire lack of heat-transfer data at low temperatures for the compressed gases air, nitrogen, and oxygen. The data available for interchanger design are old and have been taken at room temperatures or higher for pressures in the case of air of about 16 atm. It was therefore necessary to attempt an extension of the equation recommended by Dr. McAdams (4). About 1943 the results of some measurements of transfer coefficients by Professor W. F. Giauque (1) became available, and these fortunately confirmed the essential reliability of the modified McAdams equation. The need is considerable, however to extend the measurement systematically for pressures ranging from 50 to 200 atm. and temperatures from room temperature to near the critical temperature of each gas. It is also important to obtain coefficients for the heat transfer of flowing liquid gases such as oxygen, nitrogen, and air at several higher pressure levels. Professor Giauque has measured the transmission coefficients for boiling liquid oxygen and air, and the values were most welcome for design. They will doubtless become a part of the scientific literature in due course.

A problem which has received much less attention than is desirable is the determination of the heat-transfer characteristics for other than circular-section channels. Thus, annular channels with and without bonded straight and spiralled spacers, the circular section with bonded twisted copper ribbon, the singly and multiply connected coiled high-pressure encased types and feed precoolers used in the S-units, and other types are amenable to design at present only through the use of McAdams' equation 4c, and the use of the hydraulic radius concept. Systematic tests at low temperatures and under pressure conditions common in the low-temperature field would after correlation place the design of these important interchanger types on a sound basis and give the designer confidence in introducing novel designs of heat-transfer equipment as occasion arose.

In the course of the design of the J–T–S interchanger and the subsequent checking of the design through temperature readings of the fluid streams along the

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than the triple point of argon. Accordingly, if the solubility is small enough a concentration of argon is conceivable in the column at a temperature corresponding to the triple point where crystals of argon would not only separate but accumulate. A column at a pressure of 1.68 atm. would have an effluent temperature of about 83.7°K., corresponding closely to the triple-point temperature of argon (83.91°K.), and argon crystals could scarcely form unless solid argon were quite insoluble in liquid nitrogen or the equilibrium liquid nitrogen–oxygen mixture at the top of the simple column.

interchanger, it became clear that the heat transferred at the cold end of the interchanger is far greater than would be predicted on the basis of the McAdams equation. It will be observed that both streams are in the gaseous state but the high-pressure air stream is of great density and great fluidity. It seems not unlikely that the cause of the increased heat interchange beginning at the cold end and dying out rapidly is due to a turbulence induced particularly in the high-pressure gas by the very large temperature difference which at the extreme cold end is 75°C. with a column pressure of 12 p.s.i.g. Empirically the behavior of one type of interchanger is as though the heat-transfer coefficient decreased from the cold end in accordance with the algebraic form

$$H = H_n \times 10^{c(1 - z/l)^4}$$

where z is the distance reckoned from the cold end for an interchanger of total length l, and H_n is the normal over-all coefficient calculated, for example, by McAdams' equation. The experience suggests the need of investigating heat-transfer coefficients for large temperature differences where heat is being transferred between channels bearing dense gases. The measurements should also be extended to include liquids under pressure, a practical case in point being the boiler coil design.

There is also the incompleted general problem of the formulation of design procedure for the J–T–S interchanger. Two-channel interchangers often offer sufficient difficulty, and the three-channel case illustrated by the pump unit exhibits enhanced difficulty of attaining a satisfactory solution, for it is known that the transfer coefficients, the viscosity, and the heat conductivity vary with temperature as do also the heat capacities of the fluids, particularly high-pressure gases. A part of the general problem is also the calculation of the allowable thickness of the metal barriers along which heat must flow in order that heat flow over the interchanger section may take place without unduly large or irregular temperature differences. The application of the standard heat-flow theory to these cases could be made, but with a better knowledge of surface heat-transfer coefficients many cases could be solved completely. The heat conductivity of some metals such as copper, it is worth mentioning, changes rapidly as lower temperatures are reached and from 20° K. down very rapidly indeed.

Of course there is a great lack of knowledge of the viscosity as a function of pressure at low temperatures for gases and an even greater lack of heat-conductivity values, data which are essential for the correlation of heat-transfer coefficients.

A most interesting situation which is still in a far from satisfactory state is the extension of our knowledge of the equilibrium properties of the ternary mixture nitrogen–oxygen–argon. The amount of confirmed published knowledge is far from extensive and the results have a high practical value.

There is also the interesting question of the solubilities and mixture properties generally of the rare gases apart from argon. Such knowledge as exists forms the basis now for the extraction of these gases, supplied by the Linde Company and the Air Reduction Company, but extended knowledge of the properties of these mixtures will inevitably lead to improvements in processes and greater availability to satisfy the increasing practical uses of the rare gases.

The thermodynamic properties of air are fairly well known (2), at least relative to nitrogen and oxygen. A considerable amount of additional data is, however, needed to compile definitive thermodynamic charts covering the liquid and gaseous phases to 200 atm. for the gases comprising the atmosphere.

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METALLIC FILM FORMATION AT LOW TEMPERATURES[1]

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Apparatus and method for condensing, under approximately isothermal conditions, thin films from a molecular beam of pure lead at temperatures down to 14°abs are described. The electric conductivity of these films is measured *during* and *after* exposure to the beam.

The onset of conductivity depends upon the temperature of the film formation and is found for hydrogen temperatures at a statistical film thickness of only two atomic layers.

After exposure these films undergo substantial changes, which depend upon temperature and are determined by two mutually opposing trends: (*a*) destruction of film coherence by coalescence into isolated globules of lesser thermodynamic configuration potential—predominant *above* 100°abs.; (*b*) transition into a molecular configuration of higher conductivity—predominant *below* 100°abs.

The results, in particular with respect to the nature of trend (*b*), are discussed in the light of hypotheses by Kramer and Suhrmann and one suggested by the authors.

I. GENERAL CONSIDERATIONS

The properties of thin films of metals deposited *in vacuo* center mainly around the problem of the stability of molecular (or atomic) configuration under the varying predominance of surface forces which counteract the attainment of the thermodynamically most stable arrangement of the molecules in more or less perfect crystalline array.

Consequently, in each particular case the properties depend to a very large degree upon the conditions under which the films are formed and subsequently observed. Since the properties of such films are dependent upon the relative stability of a particular molecular configuration on a surface of physically and chemically different nature (not dissimilar to adsorption phenomena), the temperature at which the films are formed is of major importance. It follows that in order to maintain quasi-stable film configurations for study and observation, such investigations should be preferentially conducted in the low-temperature range.

It has been the purpose of the investigations summarized in the following to investigate film properties from this particular point of view.[2]

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[1] Presented at the Symposium on Low Temperature Research which was held under the auspices of the Division of Physical and Inorganic Chemistry at the 109th Meeting of the American Chemical Society, Atlantic City, New Jersey, April, 1946.

[2] These investigations were conducted at this laboratory during the period 1931–41 and are described in detail in the Ph.D. theses and published articles listed below.

Anderson, A. B. C.: "Resistivity and recombinations in extremely thin metallic layers," 1933.

Foster, M. G.: "Conductivity and mobility of thin lead films," 1939.

Armi, E. L.: "Electrical conduction and crystallization phenomena in thin lead films at temperatures between 14°K. and 500°K.," 1941.

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While extremely thin films can easily be produced by a variety of methods (chemical, electrochemical, cathodic sputtering, etc.), only deposits from the vapor phase, i.e., from a molecular beam under the purest possible vacuum conditions, are known to permit reproducible results which can lend themselves to interpretation.

In the existing literature of the field there are numerous indications of the extreme delicacy of such films, manifested by changes of properties caused by exposure to radiation, electron impact, and even small electric currents through the films; hence serious consideration has to be given to the physical means by which the properties of such films can be measured, so that disturbances of the film structure by the process of measurement are avoided as much as possible.

The determination of the electric conductivity with the use of minimal current densities (electrometric methods) has therefore been used, because it is the possibly least disturbing means of observation and also represents a singularly sensitive tool for the registration of alterations in film configurations. On the other hand, the obvious disadvantage inherent in the indirectness of the indications and consequent uncertainty of interpretation is somewhat compensated by the unusual sensitivity, since conductivity changes involving factors of 10^9 or more can be observed within short time intervals under sufficiently carefully controlled experimental conditions—an order of magnitude rarely available in measurements of other physical properties.

In view of these considerations, the experimental method and procedure were designed in the following studies to fulfill a number of desiderata: (*a*) The metal deposits should be formed at low temperature by condensation from the vapor phase (i.e., from a molecular beam). (*b*) The temperature at the surface at which the condensation occurs, i.e., the temperature at which the deposit is forming must be defined and measurable, at least approximately. (*c*) The rate of condensation must be so low that an adequate transfer of the thermal energy of the arriving molecule through the surface of condensation is accomplished in order to keep the temperature of film formation constant and as low as possible (isothermal condensation). Constancy and uniformity of beam configuration and intensity (number of arriving molecules per unit time and area) must be accomplished in order to permit the determination of the average thickness of the deposited film. (*d*) The surface upon which the film is formed must be of reproducible nature. (*e*) The possibility of determining conductivity variation continuously over an order of magnitude of 10^9 is required.

II. APPARATUS AND PROCEDURE

The vacuum vessel within which the metal was evaporated and subsequently condensed was arranged vertically (figure 1). The lower half contained furnace, collimator arrangement, and a magnetic shutter for the molecular beam, while the upper half supported the cryostatic assembly for the condensation. This glass vessel was about 50 cm. long and 9 cm. at the widest part, and the beam path had an approximate length of 15 cm.

The metal was evaporated from a furnace which had been specially designed (modification of construction previously published (4)) to maintain a uniform temperature throughout the furnace and the metal and had considerable heat capacity (thermal stability). It carried in the center of the metal charge an insulated thermocouple permitting the determination of temperature near the evaporating metal surface in the working range between 400° and 600°C.

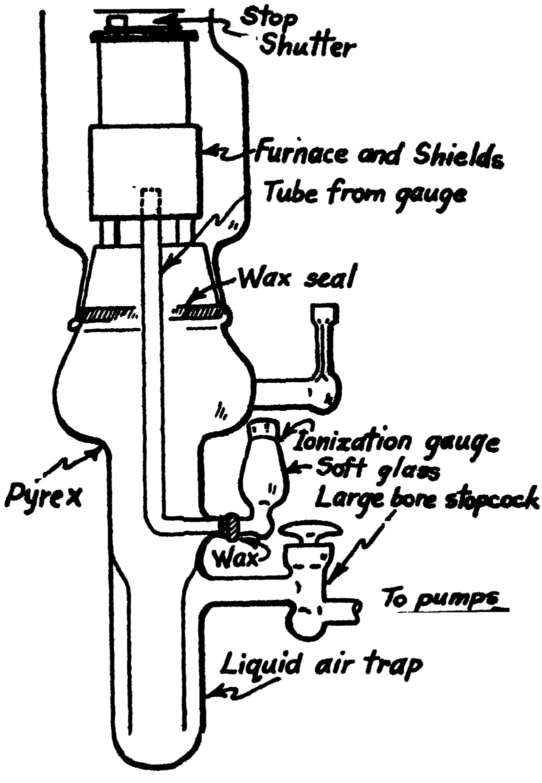

Fig. 1a

Fig. 1. (a) Schematic section through lower part of vacuum vessel. (Note: the tube leading to the ionization gauge is close to the furnace as the most probable source of residual gases.) (b) Schematic section through furnace, shield, and shutter assembly.

This furnace was encased in a tubular shield in order to restrict the molecular beam to the area of condensation, without exposing the latter to the penumbra of the beam. (The latter precaution is necessary in order to avoid the possibility of inhomogeneity.) This collimating device carried also a magnetically operated shutter which, when closed, protected the condensation plate positively against impact by random molecules evaporated from the furnace.

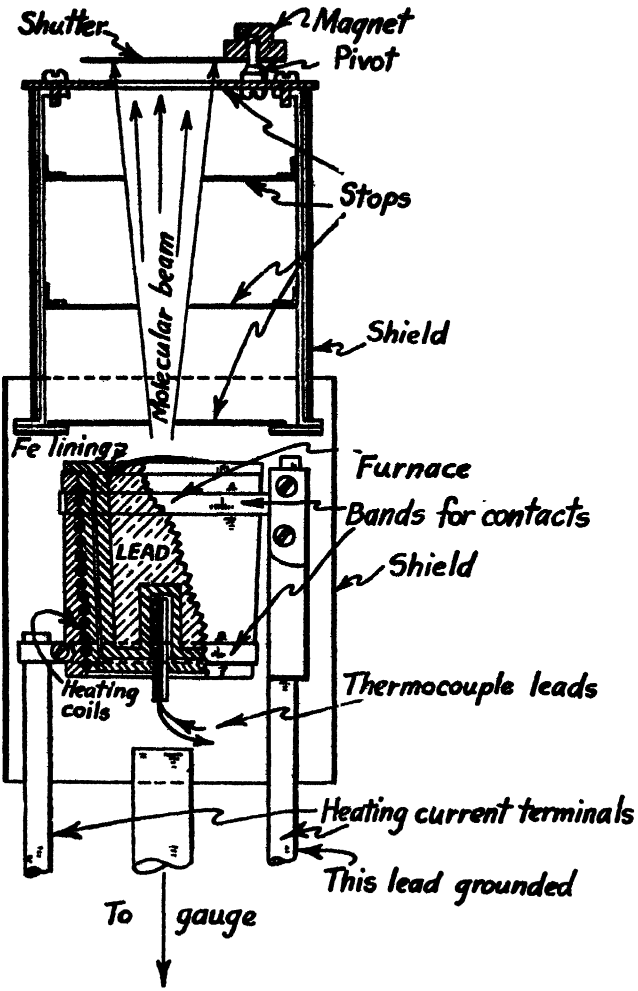

FIG. 1b

Considerable pains had to be taken in order to fulfill conditions (*b*) and (*c*).[3]

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[3] As a base for condensation thin glass slides (micro coverglass 0.15–0.20 mm. thick) were used and were put through the customary rigorous chemical procedure of cleaning. The somewhat difficult but very significant establishment of very good thermal contact between plate and cryostat was accomplished by soldering a thin plate of cast iron (thermal expansion coefficient similar to that of the glass used) to the copper bottom of the cryostat and by soldering the other side of this plate (after copper plating to produce adequate anchorage for the solder) to the glass plate, the back of which was previously platinized and electrolytically copper plated. The soldered joint between the glass and cast-iron backing was produced after final outgassing and evacuation of the whole apparatus by means of heating with high-frequency induction.

The cryostat consisted of a thin-walled copper container with flat bottom to which the above condensation assembly was attached. This container was suspended in the vacuum vessel by a long thin-walled German-silver tube through which it could be filled. This tube was attached to the vessel by a large ground metal cone arranged for water circulation in order to prevent thermal strain at

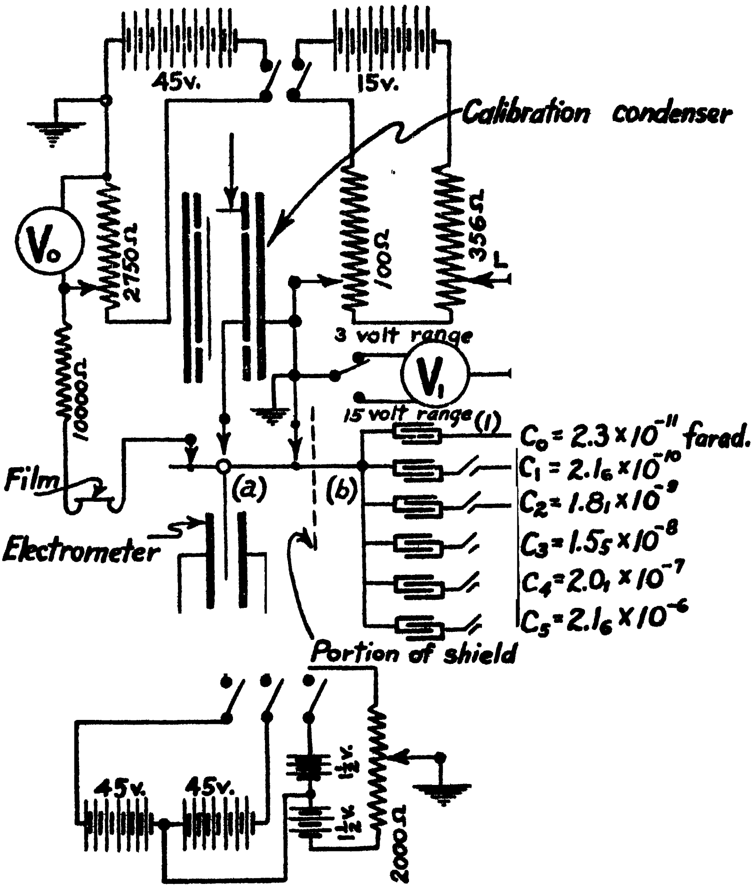

FIG. 2. Circuits for measurement of film resistances

the junction between metal and glass by transfer of cold from the evaporating cooling agent.

The cryostat could be connected through a Dewar siphon with containers for liquid air or hydrogen, and was also equipped for the reduction of the boiling temperature by lowering the pressure.

The electric contact with the film was made by platinizing sections of the exposed side of the glass plate, leaving only an area of 2 cm.^{2} free for the section of the condensed film on which the conductivity was measured.

It was also considered a matter of major importance to shield the surface, particularly during the outgassing period, against condensation of impurities, and this was accomplished by applying a second shutter in front of the glass plate. A thermocouple at the plate made it possible to measure approximately the temperature changes occurring during exposure to the beam.

The method for measuring the electric conductivity was as follows (figure 2): A known potential E_1 charged a known capacity C by leakage across the film. An opposite potential, E_2, compensated the charge of the condenser and a sensitive string electrometer was used as null instrument. One or more of a set of six condensers with capacities ranging from 10^{-11} to 10^{-6} F could be inserted into the circuit so that a change in conductivity over the order of magnitude of 10^9 could be measured almost continuously and in short time intervals. The resistance of the film is then given by: $R = tE_1/CE_2$.

The equipment for and the procedure of evacuation and outgassing were designed and manipulated in the manner customary for avoidance of disturbance by residual gases, especially by their condensation at parts exposed subsequently to low temperature. The vacuum was measured with sensitive McLeod and ionization gauges; the outgassing of the whole apparatus, in particular of parts of it, was accomplished with induction from a 10-kilowatt high-frequency source.

As metal for the formation of the films lead of high purity was used. The reasons for the choice of lead were:

(*1*) Its melting-point and vapor-pressure curves are particularly convenient, for an adequate rate of evaporation can be obtained without resorting to high temperatures which would seriously interfere (by radiation from the furnace) with the temperature conditions at the film surface during exposure; at room temperature the vapor pressure is sufficiently low to prevent stray condensation within the apparatus.

(*2*) The high specific gravity of lead permits a fairly accurate determination of the mass of heavy deposited layers for purposes of calibration by weighing.

(*3*) Because of the high molecular weight and large atomic volume of lead, it can be expected that the molecular mobility at the surface of the condensation is relatively small.

(*4*) Lead belongs to the fourth group of the Periodic System, where most elements are characterized by the existence of conducting or non-conducting allotropic modifications and where the electron configuration is favorable for superconductivity (in view of the possibility of extending these experiments into the range of helium temperatures).

The rate of film deposit as a function of furnace temperature and length of exposure interval can be derived approximately from kinetic theory considerations for effusing molecules under mean-free-path conditions in a high vacuum. While the calculation was found to result in the proper order of magnitude—a result which indicated the absence of appreciable reflection from the surface—an actual calibration was found necessary by weighing (microbalance) film deposits formed over a long period of time under constant conditions. It was found that at a furnace temperature of 400°C. the density of the molecular beam (in g./min./cm.^{2}) was 10^{-9}, at 500°C. 10^{-7}, and at 650°C. 10^{-5}, indicating that it was easy to arrive at a rate of condensation of the order of one (statistical) atomic layer per minute at the condensation surface without resorting to delicate thermal controls of the furnace temperature.

The experimental procedure consisted—after careful evacuation and outgassing, extended over days—in bringing the furnace to thermal equilibrium at the temperature required for the desired rate of deposition. The cryostat was then cooled to the temperature required for film formation with liquid air and liquid hydrogen (if necessary under reduced pressure) and the "background" conductivity of the condensation plate was determined, which amounted to approximately 10^{14} ohms. The shutter in front of the plate was then opened and finally also the shutter of the furnace shield, so that the surface was exposed to the molecular beam while conductivity measurements were taken. After a sufficient number of atoms had been deposited, the shutter was closed and the changes which the film so deposited underwent with time at constant or varied temperature of the cryostat were followed by observation of the conductivity.

III. RESULTS AND DISCUSSION

In describing the results one has to distinguish between the conductivity observations obtained while the plate is exposed to the beam and those after the beam is shut out and the film is left to itself.

While there is common agreement among the investigators that a certain statistical thickness is required for establishing a conductivity, the magnitude reported for this quantity varies substantially with different observers who worked under approximately the same conditions. The values depend obviously upon the temperatures of formation of the film. Those found for lead are about 60 Å. at room temperature and approximately 30 Å. for liquid-air temperature, if rates of deposit of the order of 1–3 Å. per minute are employed. If the temperature of formation was in the range of the hydrogen temperatures, this thickness decreased substantially and conductivity was observed even at a thickness as low as 7 Å., equivalent to a statistical thickness of only two lead atoms (figure 3).

The conductivity of these exceedingly thin layers is instantly destroyed if the temperature is raised into the range in which tendency (*a*) prevails (see below). After, by such treatment, the conductivity is "wiped out" and the original low temperature is restored, a new layer can be formed on the surface without observable interference by the former layers. This operation can be repeated many times.

The conductivity behavior of the films *after* exposure to the beam depends upon the temperature at which the film is formed and the number of atoms contained in it, as well as the temperature to which the film is exposed subsequent to the closing of the shutter.

Films after exposure showed principally opposing tendencies:

(*a*) At a temperature above 100–120°abs. the trend is to form a non-conductive configuration (if the low-temperature film is sufficient to show conductivity initially). If such films are left to themselves, the conductivity disappears quickly until the resistance reaches infinity (background resistance). Subsequent exposures to the beam show the same phenomenon repeatedly, until a total (statistical) thickness is reached which is many times that of the thickness which first showed conductivity.

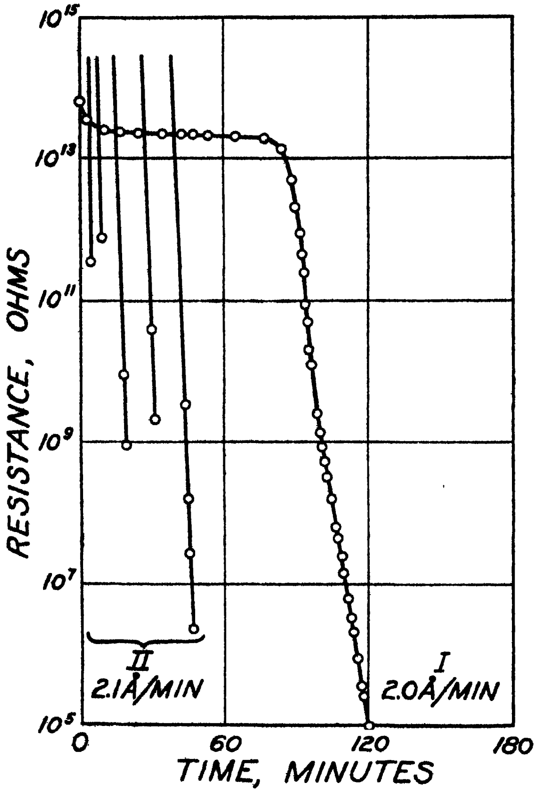

FIG. 3. Time-resistance variation during film formation: I at 290°abs.; II at 14°abs. I shows that about sixty statistical atomic layers (160 Å.) are necessary to establish the beginning of conductivity; II that at 14°abs. conductivity sets in as low as two statistical atomic layers (7 Å.) and that it can be "wiped out" and reëstablished repeatedly (five times in this case). The parallelism of II indicates reproducibility without interference by previous deposits.

The rate of disappearance of conductivity decreases with increasing number of deposited molecules. The conductivity of the film reappears and disappears upon additional exposures to the beam at a rate depending upon the magnitude of the preceding deposits and rates of condensation until a thickness is reached which maintains its conductive qualities. This thickness again depends on the temperature at which the measurement is taken and is the larger the higher the temperature.

Figures 4 and 5 represent typical demonstrations of this behavior. Figure 4 (room temperature during and after exposure at a rate of deposit of about two atoms per minute) shows complete disappearance of conductivity up to film thicknesses of seventy to eighty atoms (230 Å.), while films formed at and subsequently exposed to 90–120°abs. at a lesser rate (less than one atom per minute) do not lose their conductivity any more completely for film thicknesses of about twenty atoms (50 Å.), while the trend towards a decrease in conductivity *after* exposure still persists.

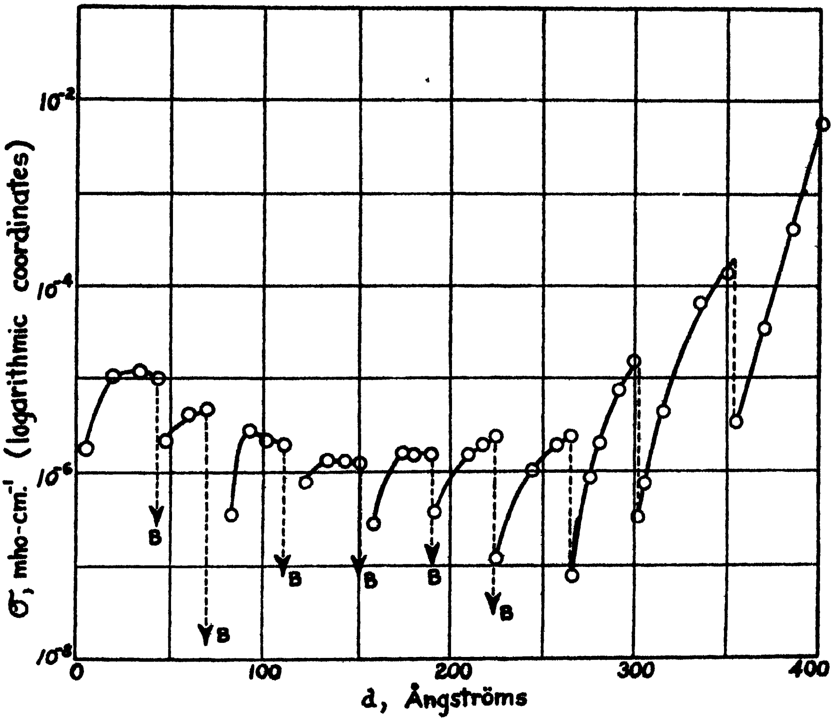

FIG. 4. Conductivity *vs.* statistical film thickness at 290°abs. for interrupted film formation at a deposit rate of 7.5 Å. per minute. B indicates complete disappearance of film conductivity (background). This disappearance continues until approximately 230 Å. are reached.

The rate of disappearance is better followed for films formed at low temperature, i.e., between 20° and 40°abs. (figure 6), and subsequently exposed to a variety of higher temperatures. It appears that this trend controls the behavior of films regardless of whether they were formed at high or low temperature.

(*b*) At temperatures of original formation and subsequent exposure below 50–100°abs. down to 14°abs., the films show a tendency opposite to the above, inasmuch as the conductivity increases under proper conditions rapidly over a remarkably large order of magnitude. For instance, in figure 7 (curves I and

II) the resistance was found to decrease by a factor of about 5000 within 75 min. after exposure. This behavior is only observable if, as a paramount condition, contamination by gas condensation on the surface is avoided, since the metallic properties of films of this type are exceedingly sensitive to any sort of surface disturbance, which always acts destructively upon conductivity.

Trend (*b*) is definitely temperature dependent, as evident particularly from curves I and II in figure 7, where the rate increased substantially when the film was heated from 14°abs. to 90°abs. or respectively from 20°abs. to 50°abs. and then from 50°abs. to 90°abs.

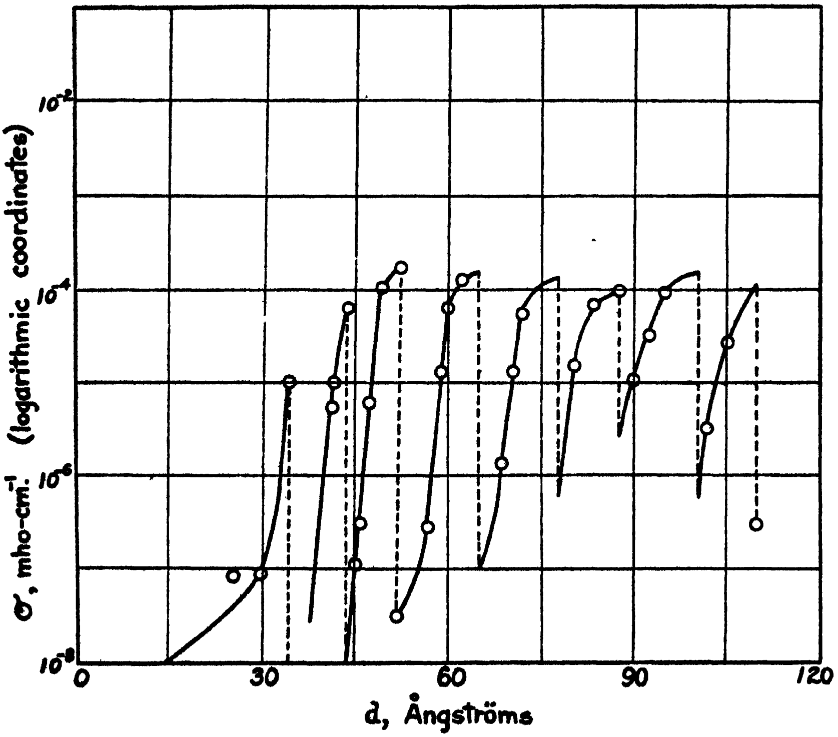

FIG. 5. Conductivity *vs.* statistical film thickness at 90°abs. for interrupted film formation at a deposit rate of 2 Å. per minute. Complete disappearance is only observed up to 50 Å.

The transition from the temperature range in which the two opposing tendencies prevail is not sudden, but extends over an interval in which both may even balance each other so that a certain stability may be apparent. This transition temperature depends obviously upon the number of atoms contained in the film in the sense that fewer atoms seem to expose trend (*a*) already at lower temperature, provided the latter is above 90°abs. The reverse appears to be true for tendency (*b*): for slightly thicker films trend *a* can prevail above 90°abs.

It is also significant that a deposit formed in the range (*a*) will not show the tendency (*b*), if rapidly cooled after deposit; in other words, the tendency (*b*) has been observed only in layers formed at a low temperature.

This observation does not hold for films formed at low temperature and subsequently exposed to the trend *a* for a time interval insufficient for complete destruction of conductivity. In this respect curve I in figure 6 may serve as an example. Exposure to 110°abs. for 10 min. shows trend (*a*), and subsequent exposure to 65°abs. trend (*b*); heating for about 10 min. to 140°abs. alters the trend again and strongly to (*a*), while subsequent cooling to 90°abs. and 65°abs. reverses the trend to (*b*), until final heating to 175°abs. destroys the conductivity irreversibly.

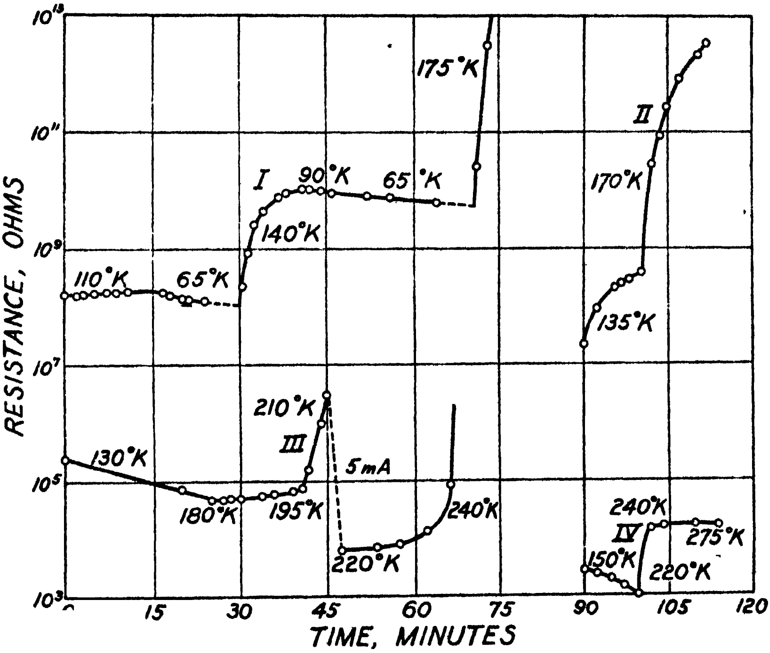

FIG. 6. Time–resistance variation after exposure to temperatures above 90°abs. The temperatures after exposure are practically all within the realm of trend (*a*) (resistance increases with time).

A substantially heavier film (curve III) at 130°abs. still shows trend (*b*), and heating to 180°abs. is required to produce a (not very large) reversal.[4]

This complex behavior indicates, obviously, the existence of two mutually contradictory stabilities of configuration, of which one (tendency *a*) is obvious from thermodynamic considerations and has been reported by numerous observers (1, 2, 8, 10, 11, 14): the thermodynamic potential of the deposit of a few statistically arranged atomic layers produces the tendency for a configuration exposing lesser surface and containing, at least over limited realms, a higher degree of order (partial lattice formation). This more stable configuration will be one of globules (droplets) of semicrystalline character.

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[4] Though not the subject of specific discussion in this presentation, it may be mentioned that in the case of film III a current of 5 milliamperes was passed through from a separate source for about 3 min.; this decreased the resistance by a factor of about 90 without destroying the sensitivity of the film to trend (*b*).

This type of configuration will render a coherence of the film, even in the sense of a few bridges, improbable as long as the original deposit contained a relatively small number of atoms. This lack of coherence is manifested in the disappearance of the conductivity.

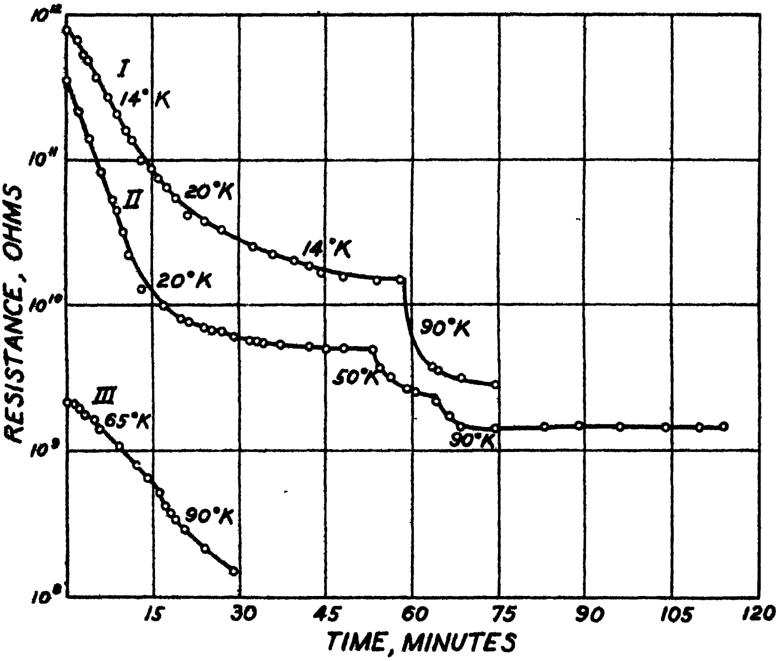

FIG. 7. Time-resistance variation after exposure to temperatures below 90°abs. The temperatures after exposure are all within the realm of trend (*b*) (resistance decreases with time).

The rate at which this transition occurs from a statistically arranged condensate into the semicrystalline globule depends obviously on the mobility of the molecules on the surface, and it appears remarkable that at temperatures of approximately 170°abs. the mobility of the lead atoms is still so large as to cause a disappearance of conductivity at the rate indicated in figure 6 (curves I and II).

It should, however, not be overlooked that this tendency, based upon a high mobility of lead atoms at fairly low temperatures, can only exist if it compensates sufficiently the surface forces which produce adsorption, which should have the tendency to "spread" the molecules of a deposited layer into a configuration of fairly uniform occupancy of the surface (as long as the number of molecules is sufficiently small to be still subject to the surface forces). The cause for this apparent inactivity of the surfaces may be that, in spite of all efforts to outgas the condensation surface previously, adsorption of sufficiently available residual gas molecules at low temperature has already annihilated the surface activity (saturation of the van der Waals forces), so that the condensation of the lead molecules occurs on a "compensated" surface.

The cause of trend (*b*) is less obvious than of (*a*); the experiments show that it is only observed on films formed at low temperature, i.e., for layers which during formation have not been subject to trend (*a*). The phenomenon must thus be associated only with molecular configurations which have not yet been transferred into the quasi-crystalline state of isolated globules. Neither can trend (*b*) be interpreted by the absence or restriction of molecular mobility at sufficiently low temperatures and a consequent inability to coalesce, since definite changes do occur after exposure to the beam. In other words, if only absence of coalescence were the cause, a definite conductivity should be associated with a definite number of molecules in the film and no further change after the exposure should be expected.

Several observers (3, 6, 7, 9, 14, 15) have also reported an increase in conductivity, but a definite distinction between the behavior during and after film formation at low temperatures is in general not made. This distinction appears to be of particular importance in view of an interpretation of this trend. Two different types of reaction causing it can be offered,—one based purely on the geometry of the configuration, the other on intermolecular changes.

The former must postulate that, instead of the high-temperature tendency to form a configuration of isolated globules which disrupt the film continuity, at low temperatures a different type of (thread-like) structure prevails, the formation of which assists the establishment of conductive bridges. The probability of this interpretation appears restricted.

The other type of explanation must assume the existence of a molecular film configuration for low-temperature deposits which possesses, in spite of physical coherence, either no or only restricted metallic qualities. One possibly not too far fetched hypothesis would be this: condensation from the molecular beam at sufficiently low temperature results in a statistical surface deposit wherein the molecules are still in the non-metallic state in which they existed in the vapor phase of the beam. The individual molecules are separated from each other by potential barriers which cannot be overcome because of lack of thermal energy available under the conditions of closely isothermal low-temperature condensation (conditions (*a*)–(*c*); see above). Since, however, the activation potential required for the intermolecular transition into the conductive phase is probably very small, even a temperature of 14°abs. (which is probably much higher locally at the instant of molecular impact) may not be low enough to avoid this transition completely, and the majority of the (very slowly) deposited mole will require a considerable amount of time for this transition. Trend (*b*) wou thus be caused by a gradual transition from a non-metallic into a metallic state by the establishment of an electron configuration within the film, apparent by a gradual increase in conductivity. This finally completely established state is maintained as long as the film temperatures remain sufficiently low to prevent significance of trend (*a*), i.e., coalescence.

The suggestion of a transition from an amorphous non-metallic into a crystalline metallic phase was first made by J. Kramer (3, 6, 7, 15) and his school and was based upon his observation of sharply defined transition temperatures of the type known for allotropic transformations. Several other investigators have not been able to confirm the general validity of this assumption; it is obviously incorrect for our observations of lead. At the same time they demonstrate, however, that if lesser precautions for the control of the film temperature during and after exposure had been taken, a sharp instead of a gradual transition into the conductive state could easily have been recorded, in view of the large temperature dependence of trend (*b*) (e.g., curve I in figure 7). There is little doubt that this interpretation is correct for certain elements of lesser metallic character of which non-metallic "amorphous" modifications are known to occur already at room temperature, e.g., antimony and arsenic.[6]

A not dissimilar interpretation of the nature of trend *b* has been suggested by Suhrmann and his collaborators (13): the increase in conductivity at low temperatures is due to a transition from a state of lesser to one of higher order of molecular configuration, the latter being the better conductor. An activation energy of the order of 150–800 cal. per gram-atom, characteristic for each metal, is required for this transition. Obviously this type of statistical transition does not require a defined transformation point and differs thus from Kramer's assumption.

Suhrmann's hypothesis is analogous to the one suggested in this paper, but differs in the apparent assumption of metallic properties for the original film deposit in the state of low order. However, it seems difficult to account for the magnitude of the conductivity changes observed under these conditions solely with a transition from a disordered to an ordered state.

Since films which show this behavior are exceedingly delicate and unusually sensitive to external disturbances, attempts to study this state by electron diffraction may prove futile. On the other hand, it is hoped that adequate techniques can be developed to form and observe such films at helium temperatures, particularly with regard to the occurrence of superconductivity. If, according to the above (and also Kramer's) suggestion, the low-temperature film consists of mutually isolated lead molecules and is thus essentially nonmetallic in character, it should, even for considerable thickness, not become superconductive, for the same reason that, in contradistinction to β-tin, α-tin is not a superconductor. If, according to Suhrmann, the molecular properties are already metallic but the array one of disorder, it may be expected that for sufficiently low temperatures superconductivity will be observed.

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[6] In spite of the absence of a defined transition temperature, it is not excluded that for the case of lead a true α-modification of non-metallic character and stable only at very low temperature exists in the film at these particular conditions of condensation and that the increase of conductivity would be caused by a gradual transformation into the β-modification, so far known only for lead. The transformation rate could safely be assumed to be very low, if the transformation point should lie somewhat above 14° abs. This would be a very close analogy to the existence and behavior of the α- and β-modifications of tin, the vertical neighbor of lead in the fourth column of the Periodic System. The other elements of this column—with the probable exception of silicon—show the same type of allotropy: a non-conducting form unstable at high temperature, and a β-form with at least semimetallic [illegible]rties, well known for carbon (diamond-graphite) and recently established for [illegible]manium by Koenig (5).

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